ELECTRODEPOSITION ON SUPERALLOY SUBSTRATES: A REVIEW

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The present paper reviews various types of coatings, including platinum, platinum alloys, palladium, ruthenium, iridium, nickel, nickel alloys and composite coatings, on superalloy substrates using electrodeposition method. Attempts were carried out to represent an overall view of plating conditions and electrolyte and highlight the importance of the layer regarding to the performance of high-temperature coatings applied on superalloys, which is extensively used on gas-turbine components.

Keywords: Electrodeposition; superalloy substrate; coating; high temperature.

1. Introduction
Nickel-based superalloys, which are extensively used in gas-turbine engine components, require protection against high-temperature oxidation during operation. In order to protect nickel-based superalloys from oxidation and hot corrosion, diffusion aluminate coatings are widely used.\textsuperscript{1,2} Being used since 1950s, aluminate coatings based on the $\beta$-NiAl phase deposited by the chemical vapor deposition (CVD) method do not meet the requirement of the oxidation resistance at high temperature. In this regard, Pt-modified aluminate coatings can protect blades from oxidative gases even at temperatures above 1400°C.\textsuperscript{3} It is reported that addition of Pt and some of the platinum group metals (PGMs) in the aluminate coatings causes formation of some phases (such as the PtAl$_2$ phase in Pt-modified coatings) in the coating microstructure.\textsuperscript{4,5} The low ductility of these phases and large difference of thermal expansion coefficients between the substrate and PGMs causes coating degradation under the cyclic thermal stress.\textsuperscript{3,6–9}

These coatings were prepared by electrodeposition of a thin (few-micron-thick) layer of platinum or PGM and subsequent aluminizing by pack cementation or CVD. Therefore, the electrodeposition of such metals and alloys is our interest because of their important role and mission to improve the temperature resistant coatings, considering their high melting temperature, excellent chemical stability and low oxygen diffusivity.\textsuperscript{10,11} Recent investigations carried out on high-temperature coatings, especially diffusion and overlay coatings, demonstrated that electrochemical deposition of thin layer (3–7 μm) of a specific coating would enhance the service life of high-temperature coatings at elevated temperatures. For example, it was reported that electrodeposition of...
thin (few-micron-thick) layer of platinum enhances the aluminide diffusion coatings. This process improves the service life of the aluminide coatings up to three times.\(^{12}\) In the case of aluminide coatings, the aluminum reacts with platinum to form platinum aluminate, finally leading to the formation of \(\beta\)-NiAl phase. It was also reported that the formation of PtAl\(_2\) phase at the interface of coating/superalloy phase. It was also reported that the formation of aluminide, finally leading to the formation of aluminum reacts with platinum to form platinum etc.

During electrodeposition process, which are regarding the formation of surface oxide films. Such films indicate particular problems and difficulties during electrodeposition process, which are regarding the adhesion of plated films. Thus, special cleaning and processing are required to eliminate these oxides and surface films prior to plating.\(^{14}\) There are different types of surface activation and preparation before electrodeposition process. ASTM B343 (Standard practice for preparation of nickel for electroplating with nickel\(^{15}\)), ASTM B558 (Standard practice for preparation of nickel alloys for electroplating\(^{16}\)) and ASTM B254 (Standard practice for preparation and electroplating on stainless steel\(^{17}\)) are the examples of various standards and procedures carried out before electrodeposition. Authors use various methods to activate and prepare superalloys before deposition, such as using anodic etching in a specific activation solution containing 55–80 vol.% of 95–98% sulfuric acid (\(H_2SO_4\)) and 1–10 vol.% of 52% hydrofluoric acid (HF). This type of activation, where the samples are employed as the anode and using an inert cathode such as lead, is suitable for activating stainless steels-, nickel-, cobalt- and iron-based superalloys. It is also reported that an intermediate rinsing with water before electrodeposition tends to decrease adhesion of the metal deposited to the substrate. Therefore, the substrate can be preferably electroplated directly following the activation treatment. The preferred aqueous activating bath and conditions for this process are 65 vol.% of 95–98% \(H_2SO_4\) and 5 vol.% of HF at 30 Adm\(^{-2}\) and 20°C for 1 min.\(^{14}\) Some researchers prepared their samples through mechanical polishing using emery paper down to 2000 grit. To do so, they first degrease the samples with acetone in an ultrasonic bath for 10 min and then immerse them in a 30 wt.% hydrochloric acid solution at 30°C for 5 min.\(^{15}\)

Another surface preparation for nickel-based superalloys was carried out by mechanical polishing with SiC paper up to 600 grit and degreasing with acetone for 10 min in an ultrasonic bath and then thoroughly cleaning the surfaces with \(NaOH\) solution (1 molL\(^{-1}\)) for 3 min and hydrochloric acid (HCl) solution (1 molL\(^{-1}\)) for 30 s in an ultrasonic bath.\(^{18}\)

According to Zagula-Yavorska and Sieniawski, surface degreasing, surface etching, rinsing in cold water and surface activation are the consecutive steps for surface preparation.\(^{3}\) In their work, degreasing was carried out in gluconate electrolyte at a temperature of 50°C, where the electrolyte containing 180–240 gl\(^{-1}\) sodium gluconate (\(C_6H_{11}NaO_7\)) and 18–240 gl\(^{-1}\) sodium hydroxide (\(NaOH\)). Next, rinsing step was conducted in hot water in order to clean the samples‘ surface from \(C_6H_{11}NaO_7\) and \(NaOH\).
Finally, surface activation was carried out using etching in a mixture of $90 \text{ gl}^{-1} \text{HF} + 530 \text{ gl}^{-1} \text{HNO}_3$. In another work, Zagula-Yavorska et al.\cite{18} prepared their substrates using degreasing, electrolytic etching and surface activation. The degreasing was performed using $60 \text{ gl}^{-1} \text{NaOH}$ and $30 \text{ gl}^{-1} \text{Na}_2\text{CO}_3$ at $60^\circ\text{C}$. The electrolytic etching was performed in a bath consisting of $100 \text{ gcm}^{-3} \text{H}_2\text{SO}_4$ and $20 \text{ gcm}^{-3} \text{NaCl}$ at room temperature. Besides, surface activation was done in a bath comprising $20 \text{ gcm}^{-3} \text{NiCl}_2$ and $120 \text{ gcm}^{-3} \text{HCl}$ at room temperature. Saremi and Bahraini\cite{19},\textsuperscript{,19} firstly, treated their samples anodically in concentrated $\text{H}_2\text{SO}_4$ ($65$–$70\%$) at room temperature and at anodic current density of $20 \text{ Acm}^{-2}$ for $1\text{ min}$ to provide the required roughness (based on ASTM B558). Table 1 illustrates the different surface preparations in brief.

### 3. Platinum Electrodeposition

Electrodeposition of platinum is practicable using chloride, ammine, sulfate–nitrite and hydroxyl complexes. Since platinum promotes hydrogen evolution reaction (HER) considering the good catalytic activity of freshly deposited platinum and, on the other hand, hydrogen in its turn has very low overpotential for HER on Pt, generally, application of high current density during Pt plating is impractical.\cite{20}

There are many types of plating bath for Pt in the literature. The oldest one dates back to a French patent granted to Pilet in 1883, where platinum exists in the bath solution as chloroplatinic acid, $\text{H}_2\text{PtCl}_6 \cdot \cdot \cdot 6\text{H}_2\text{O}$, commonly referred to as “platinum chloride”\textsuperscript{.21} This type of plating bath was reported practical for $2.5$–$3.5 \text{ Adm}^{-2}$ current densities and with $15$–$20\%$ cathodic current density.\cite{20} Literature review also indicates that using $(\text{NH}_4)_2\text{PtCl}_6$ as the source of Pt with sodium citrate and ammonium chloride as supporting electrolyte and complexing agent, the current efficiency increases up to $70\%$ with low applied current density.\cite{20} Crack-free crystalline layers of platinum can be deposited from these baths up to a thickness of $20 \mu\text{m}$ at a temperature range of $45$–$90^\circ\text{C}$.

Regarding the electrodeposition of platinum on superalloy substrates, there are widely-used common Pt plating electrolytes, as an electrolyte system based on a platinum salt named dinitrodiammineplatinum known as P-salt, $\text{Pt(NO}_2)_2(\text{NH}_3)_2$ (see Refs. 22–24) and $[(\text{NH}_3)_4\text{Pt(HPO}_4)_2]$, known as Q-salt,\textsuperscript{25,26} which are reported in several classical papers and patents.

### Table 1. Surface preparation of superalloys and activation phenomena.

<table>
<thead>
<tr>
<th>Degreasing</th>
<th>Supplementary activation</th>
<th>Conditions</th>
<th>Substrate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degreasing in electrolyte containing $180$–$240 \text{ gl}^{-1} \text{Na}_2\text{CO}_3$ and $18$–$240 \text{ gl}^{-1} \text{H}_2\text{SO}_4$ at $60^\circ\text{C}$.</td>
<td>Activation in the mixture of $90 \text{ gl}^{-1} \text{HF} + 530 \text{ gl}^{-1} \text{HNO}_3$.</td>
<td>—</td>
<td>Inconel-713 LC</td>
<td>3</td>
</tr>
<tr>
<td>Degreasing with acetone in an ultrasonic bath for $10\text{ min}$.</td>
<td>Activation in $30% \text{ HCL}$.</td>
<td>At $30^\circ\text{C}$ for $5\text{ min}$.</td>
<td>TMS-75</td>
<td>6</td>
</tr>
<tr>
<td>Degreasing with acetone for $10\text{ min}$ in an ultrasonic bath.</td>
<td>Activation firstly in $1 \text{ M NaOH}$ and then $1 \text{ M HCl}$ solution.</td>
<td>$1\text{ min}$ for NaOH and $30\text{ s}$ for HCl.</td>
<td>TMS-82t</td>
<td>8</td>
</tr>
<tr>
<td>—</td>
<td>Activation in a mixture of $65% \text{ H}_2\text{SO}_4$ and $5% \text{ HF}$.</td>
<td>$30 \text{ Adm}^{-2}$ and $20^\circ\text{C}$ for $1\text{ min}$.</td>
<td>General (US patent)</td>
<td>14</td>
</tr>
<tr>
<td>Degreasing with sodium hydroxide $60 \text{ gl}^{-1}$ and sodium carbonate $30 \text{ gl}^{-1}$. Electrolytic etching with $\text{H}_2\text{SO}_4 100 \text{ gcm}^{-3}$ and sodium chloride $20 \text{ gcm}^{-3}$ at $25^\circ\text{C}$.</td>
<td>Activation in nickel chloride $20 \text{ gcm}^{-3}$ and $\text{HCl} 120 \text{ gcm}^{-3}$ at $25^\circ\text{C}$.</td>
<td>Degreasing at $60^\circ\text{C}$. Etching and activation at $25^\circ\text{C}$.</td>
<td>Inconel-713 LC &amp; and CMSX-4</td>
<td>18</td>
</tr>
<tr>
<td>—</td>
<td>Activation in concentrated $\text{H}_2\text{SO}_4 (65$–$70%)$.</td>
<td>at $20 \text{ Acm}^{-2}$ for $1\text{ min}$ at $25^\circ\text{C}$.</td>
<td>Inconel-738</td>
<td>19</td>
</tr>
</tbody>
</table>
These systems allow a maximum current density of 5 A dm\(^{-2}\). Addition of excess of sodium or potassium nitrite to chloroplatinic acid (IV) results in reduction of Pt(IV) to Pt(II) state to form the square planar complex K\(_2\)Pt(NO\(_2\))\(_4\) with evolution of nitric oxides. Hence, addition of stoichiometric amounts of ammonia leads to the precipitation of crystalline cis-Pt-(NH\(_3\))\(_2\)(NO\(_2\))\(_2\) (or Pt-P-salt). Reports demonstrated that these systems give good deposits up to 7.5 \(\mu\)m, whereas current efficiency varies from 10% to 40% depending on supporting electrolytes (ammonium nitrate, sodium nitrate and ammonia) and presence of high working temperature varying from 70°C to 90°C. Rashidghamat et al.\(^{26}\) utilized P-salt electrolyte at 91°C with a solution pH of 10–10.5 and Pt concentration greater than 12 g/l in their work. They plated hemispherical centers of Pt mostly in the form of flat deposits on Rene-80 superalloy. Their results demonstrated that deposition rate of platinum layer linearly increases with current density in the range of 0.3–0.5 A dm\(^{-2}\); however, by further increasing the current density beyond the critical amount (over 0.5 A dm\(^{-2}\)), a sharp loss in the plating efficiency was observed. Accordingly, the average coating thickness increased from 3 \(\mu\)m to 5.5 \(\mu\)m and then decreased over the critical current density to 3.6 \(\mu\)m. They have also represented that the Pt size decreased with current density, while it increased with duration of electrodeposition. Zagula-Yavorska et al.\(^{3,18}\) utilized this type of bath for Pt plating on Inconel-713LC and CMSX-4. The appropriate current density in their work was reported as 0.1 A dm\(^{-2}\) in an electrolyte with 15 g/l tetraamine-platinum. Coating surfaces after platinum electrodeposition with thicknesses of 3 and 7 \(\mu\)m had a closely spaced “cauliflower” appearance. They used titanium as an anode for electrodeposition. In elsewhere, a similar electrodeposition bath based on [Pt(NO\(_2\))\(_2\)(SO\(_4\))]\(_2\) was stated by Hopkin and Wilson in literature.\(^{22}\) Although this bath can be used for plating on many metals such as Ti, Cu even at room temperature, it is not very common for plating on superalloys. Some researchers deposited platinum from commercial bath.\(^{8,27}\) In comparison, significant developments in platinum electrodeposition have been recently carried out by Johnson Matthey, Ltd., and other scientists.\(^{27–30}\) Johnson Matthey, Ltd., patented a new bath formulation based on platinum–tetraamine complex (Tetraammineplatinum (II) dihydroxide: [Pt(NH\(_3\))\(_4\)]\(^-\)(OH)\(_2\)) in a phosphate buffer with higher cathode current efficiency, which is as useful as commercial electrodeposition bath, where high rates and thickness are required. These types of bath were found suitable for platinum plating on superalloy substrates. It is noted that high temperature is needed for the reduction of platinum, as it is essential to drive the slow ligand displacement reaction to a reasonable rate. The mechanism was shown to be stepwise replacement of ammonia ligands by water molecules. Deep fundamental studies of the mechanism and applied aspects of this new bath were conducted in the literature.\(^{31–35}\) Koslov\(^{36}\) patented the bath formulations to electroless autocatalytic plating of platinum onto a superalloy substrate such as Co-superalloy and Inconel.

It is reported\(^{37}\) that for high-temperature applications, the Pt presence in the aluminate coatings system (Pt-modified aluminate coatings) reduces void precipitation of secondary harmful phases at the interface of metal/oxide. These coatings are typically composed of dual phase structures of \(\beta\)-NiAl + PtAl\(_2\) having at least 45 vol.% of PtAl\(_2\).\(^{38}\) Figure 1 represents the cross-section microstructure of the post-heat-treated NiAl coating. Three distinct zones along the cross-section of the coating were characterized. The outer zone consists of an aluminum-rich NiAl matrix dispersed with substrate element precipitates. This zone is identified as “precipitated high aluminum NiAl” in Fig. 1.

Fig. 1. The cross-section back-scatter micrograph of the NiAl coating on superalloy substrate. Source: Reprinted with permission from Shirvani et al.\(^{38}\) Copyright: Elsevier (2012).
It has been also confirmed that Al uptake is favored by the presence of Pt at the outermost layers of the coating using a low activity process. Furthermore, the Pt content at the outer surface of the coating decreases sharply toward the substrate when longer diffusion treatments are conducted prior to aluminization. Other studies show that platinum accelerates aluminum diffusion, then reduces the vacancies flux from the metal to the surface and inhibits vacancy coalescence and internal void formation. Pt is known to enhance scale adhesion by reducing the segregation of harmful elements such as S to the scale/coating interface and/or by reducing void formation at the interface. Researchers also reported that platinum decreases the diffusive flux of alloying elements to the coating, promotes a selective alumina scale formation and accelerates healing after spallation. Pt slightly accelerates the alumina scale growth and delays transformation of metastable alumina oxides to \( \alpha \)-Al\(_2\)O\(_3\). The addition of platinum to an aluminate coating improves the stability of \( \beta \)-NiAl phase and delays the transformation of \( \beta \)-NiAl to the \( \gamma' \)-Ni\(_3\)Al phase. Table 2 presents the Pt plating bath and conditions briefly.

### 4. Platinum Alloy Electrodeposition

To improve the protective performances of the Pt-modified aluminide coatings, much attention has been paid to Pt-based binary alloy coatings, which are reported throughout the literature.\(^{43,44}\)

Pt–Ir alloy coatings from amidosulfuric acid solutions (HOSO\(_2\)NH\(_2\)) were electrodeposited on nickel-based single crystal superalloy TMS-75 using electrodeposition.\(^{45,46}\) Researchers investigated the effects of plating electrolyte temperature, current density and mole concentration ratios of \([\text{Ir}^{3+}] / [\text{Ir}^{3+}] + [\text{PtCl}_6^{2-}]\) on the deposition rate, composition and crystallographic structures of platinum–iridium alloy coatings. The composition of chloride bath used in this work is iridium chloride: \( \text{IrCl}_3 \cdot 4\text{H}_2\text{O} \) (0–40.0 gl\(^{-1}\)), chloroplatinic acid hexahydrate: \( \text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O} \) (0–55.5 gl\(^{-1}\)), amidosulfuric acid: \( \text{HOSO}_2\text{NH}_2 \) (38.0–48.0 gl\(^{-1}\)), and sodium nitrate: \( \text{NaNO}_3 \) (40.0–50.0 gl\(^{-1}\)).

The solution pH was also adjusted to 2 using 2 N HCl or 1 N NaOH. They showed that when the current density increases from 0.5 Adm\(^{-2}\) to 4 Adm\(^{-2}\), the Ir content in Pt–Ir alloy coatings increases from 23.6 at.% to 30.5 at.%. Their results also confirmed that the deposition rate of the coatings linearly increases as current density rises (Fig. 2). These results demonstrated that with increasing electrolyte temperature, the deposition rate and Ir content increases, whereas the grain size of Pt–Ir alloy coatings decreases. Dense and smooth Pt–Ir alloy films were obtained at 1 Adm\(^{-2}\) and 80°C. Pt–Ir alloy coatings with expected compositions can be readily fabricated by controlling the mole concentration ratios of \([\text{Ir}^{3+}] / [\text{Ir}^{3+}] + [\text{PtCl}_6^{2-}]\) in the electrolyte. Although detailed investigation on the structure and morphology of electrodeposited Pt–Ir coatings was also presented in their report, XRD analysis revealed that all the coated Pt–Ir films had a single phase with fcc structure, and the lattice parameters of the coatings decrease linearly with increasing Ir content. The electrochemical reductions through depositing the alloy are as:

\[
\text{PtCl}_6^{2-}(\text{aq}) + 4e^- \rightarrow \text{Pt(s)} + 6\text{Cl}^-(\text{aq}), \quad E_0 = 0.744 \text{ V}
\]

and

\[
\text{Ir}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Ir(s)}, \quad E_0 = 1.156 \text{ V}.
\]
Regarding the above reduction potentials, it is obvious that iridium can be preferentially reduced to platinum, as it is indeed observed in this investigation. The process is categorized as normal codeposition. In another report, researchers electroplated Pt–Ir alloys on the nickel-based single crystal superalloy TMS-82 by direct current technique. Figure 3 represents different morphologies of Pt–Ir electrodeposits at various current densities and different plating times. In this study, preferential deposition of Pt occurred. The mentioned study utilized amidosulfuric acid solutions in order to perform alloy plating.

Similar electrolytes were also employed elsewhere for thin film Pt–Ir plating, where it was found that when Ir content exceeds 3 at.%, Pt–Ir films exhibited the (111) preferred growth orientation. It was also found that pre-deposition of Ni and Pt promotes the deposition rate and changes composition of overlaying Pt–Ir films. The surface of Pt–Ir deposits was granular consisting of numerous nodules with mean size increased with deposition time and current density. Ir addition to Pt-modified aluminide coating can be among the solutions to retard surface rumpling. It was reported that Pt-modified samples with Ir content had a much smoother surface than the Pt-modified coatings after cyclic oxidation, where the latter suffered from severe surface rumpling. In this regard, when the Ir content exceeded 80 at.% in Pt–Ir-modified coatings, internal voids are formed during cyclic oxidation. Therefore, addition of 30–50 at.% of Ir to Pt-modified aluminized coating is most effective in enhancing oxidation resistance. Moreover, it was reported that Pt–Ir-modified aluminide coating enhances the type I hot corrosion resistance. Reports showed that factors including phase transformation from γ'-(Ni, Pt)Al to γ′-(Ni, Pt)βAl, characteristics of the scale and protection by Pt/Ir-enriched layer have important effects on hot corrosion behavior of modified aluminide coatings. Here, researchers employ binary systems since the Pt-modified aluminide bond coats are prone to rumpling, during which the thermally grown oxide (TGO) can initiate cracking, leading to spallation of the thermal barrier.

To improve the oxidation resistance of Pt-modified aluminide coatings, layered structure of PGMs such as Pt/Pd (Fig. 4) and Pt/Ru (see Refs. 58–60) were electroplated on superalloys. Pt/Pd-modified aluminide coatings also showed superior resistance to cyclic oxidation and a less rumpled surface than Pt-modified aluminide coating after cyclic oxidation. Moreover, Ru addition to Pt-modified aluminide coating is of another interest, because Ru additions to Ni-based superalloys have been shown to improve creep strength. Pt/Ru-modified bond coating consisting of 2 μm Pt + 2 μm Ru was deposited on a nickel-based superalloy by electrodeposition method, followed by conventional Al pack cementation by Song et al. The PTP-10 solution used for Pt electrodeposition contained 4–6 gl−1 Pt, 1 gl−1 cinnamic acid and 20 gl−1 NaOH. The temperature for Pt plating was controlled at 75–85°C, and the cathodic current density was 0.5–1.5 Adm−2. The Ru...
Electrodeposition on Superalloy Substrates: A Review

The plating bath contained 4–6 g l\(^{-1}\) ruthenium chloride and 50 g l\(^{-1}\) sodium sulfamate (NH\(_2\)OSO\(_2\)Na).\(^{59}\) The whole Ru plating process was performed at 50–60°C, where the cathodic current density was 1.5–5 Adm\(^{-2}\).

Researchers reported that Ru addition increases the strength of coatings and suppresses the rumpling behavior. The absence of rumpling may be responsible for the improved corrosion resistance of...
Pt/Ru-modified aluminide coating. Wang et al.\textsuperscript{61} stated that the (Ru, Ni)Al layer (Fig. 5) effectively slows down inward diffusion of Al from the coating and outward diffusion of alloy elements such as W and Mo, then suppressing the formation of topologically close-packed phases and secondary reaction zone. Table 3 represents the brief summary of deposition electrolyte and conditions for Pt alloy and layered Pt deposition.

5. Palladium Electrodeposition

Palladium coatings have technological importance, as palladium exhibits many desirable characteristics such as excellent tarnishing, wear and corrosion resistance with low electrical contact resistance and hence a wide range of applications. Palladium is deposited from many bath compositions based on simple salt PdCl\(_2\) and also from complexes such as Pd(NH\(_3\))\(_2\)(NO\(_2\))\(_2\), Pd(NH\(_3\))\(_2\)Br\(_2\), H\(_2\)PdCl\(_4\), Pd(NO\(_3\))\(_2\), Na\(_2\)Pd(NO\(_3\))\(_4\), Pd(NH\(_3\))\(_4\)(NO\(_3\))\(_2\), Pd(NH\(_3\))\(_3\)(NO\(_3\))\(_2\) and Pd(NH\(_3\))\(_4\)Cl\(_2\). Ammonia is the most suitable complexing ligand for palladium electrodeposition and most of the available literature is on ammonia complexed to palladium solely or in combination with other ligands.\textsuperscript{20} However, regarding Pd deposition on superalloy substrates, only a few types of baths have been employed by researchers. Palladium was plated from a bath containing 15 gl\(^{-1}\) Pd(NH\(_3\))\(_4\)Cl\(_2\) and 75 gl\(^{-1}\) NH\(_4\)Cl (adjusted to pH of 8 with ammonia) onto two types of superalloys (SRR99 and Rene80). Using oxidation and hot corrosion tests, researchers concluded that palladium-modified aluminide coatings show a high resistance to high-temperature oxidation and to hot corrosion. They can thus be

![Fig. 4. SEM images of Pt/Pd layers plated on Inconel-738LC. Source: Reprinted with permission from Hong et al.\textsuperscript{55} Copyright: Elsevier (2009).](image)

![Fig. 5. BSE image of the cross-section of (Ru, Ni)Al/NiAl coating on a superalloy after 2 h heat treatment in vacuum at 1050°C. Source: Reprinted with permission from Wang et al.\textsuperscript{61} Copyright: Elsevier (2011).](image)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Bath constituents</th>
<th>Substrate</th>
<th>Plating conditions</th>
<th>Thickness</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–Ir</td>
<td>IrCl(_3) · 4H(_2)O, H(_2)PtCl(_6), HOSO(_2)NH(_2), NaNO(_3)</td>
<td>TMS-75,</td>
<td>pH of 2 (using 2 N HCl or 1 N NaOH), 80°C, 1 Adm(^{-2})</td>
<td>2–8 (\mu)m</td>
<td>6 and 9</td>
</tr>
<tr>
<td>Pt–Ir</td>
<td>IrCl(_3) · nH(_2)O, H(_2)PtCl(_6), NH(_4)SO(_4)H, HCl, HNO(_3)</td>
<td>TMS-82</td>
<td>pH of 2–3 (using HCl or NaOH), 80–85°C, 0.2–2 Adm(^{-2})</td>
<td>3–5 (\mu)m</td>
<td>8, 46 and 47</td>
</tr>
<tr>
<td>Pt/Pd</td>
<td>Commercial PlatinK solution/Commercial Alpadin 300 solution</td>
<td>738LC</td>
<td>At 50°C and 1 Adm(^{-2})/at 55°C and 1 Adm(^{-2})</td>
<td>4–5 (\mu)m/ 4–5 (\mu)m</td>
<td>55–57</td>
</tr>
<tr>
<td>Pt/Ru</td>
<td>4–6 gl(^{-1}) Pt, 1 gl(^{-1}) cinnamic acid and 20 gl(^{-1}) NaOH/4–6 gl(^{-1}) Ru and 50 gl(^{-1}) sodium sulfamate</td>
<td>DZ125</td>
<td>75–85°C, 5–1.5 Adm(^{-2})/50–60°C, 1.5–5 Adm(^{-2})</td>
<td>2 (\mu)m/2 (\mu)m</td>
<td>58–60</td>
</tr>
</tbody>
</table>
considered as a feasible low-cost high-performance alternative to platinum aluminides. In another research work, Pd was electrodeposited on superalloy M38 by He et al. An electrolyte comprising 20–30 g/L Pd(NH3)2Cl2, 40–60 mL/L NH3 · H2O, and 15–25 g/L NH4Cl with respective pH, temperature and current density of 9.0–9.5, 15–50°C and 0.4–0.6 A dm⁻² were used in their work. Based on oxidation test results, they concluded that Pd-modified aluminizing coatings are obviously better than conventional aluminide coatings and as good as commercial platinum-modified coatings under the same conditions. They also stated that palladium not only stabilizes the protective alumina formed in cyclic oxidation and dramatically increases the hot corrosion resistance of the coatings, but also increases the lifetime of the β-phase by impeding the outward diffusion of substrate elements. Palladium with 3 and 7 μm thicknesses was plated using the electrodeposition process on Inconel-713LC superalloy, in the bath of palladium chloride PdCl2: 10 gcm⁻³, sulfamates acid H₂NSO₃: 100 gcm⁻³, hydrochloric acid HCl: 20 gcm⁻³ and ammonium chloride NH₄Cl: 50 gcm⁻³ at 35°C). In another work, to plate palladium on Inconel-738LC, Pd(NH3)Cl2 was used as the electrodeposition bath at room temperature by Bai et al. The thickness of the palladium layer was approximately 2–4 μm, with current density of 3 A dm⁻² for 3 min, while coatings have good adherence to the substrate without any blister and pores. Some commercial baths were also employed for electrodeposition of Pd in the literature. Table 4 represents a brief summary of palladium plating electrolytes and conditions on different superalloys substrates.

### Table 4. Brief summary of palladium plating electrolyte and conditions.

<table>
<thead>
<tr>
<th>Types of bath and composition</th>
<th>Substrate</th>
<th>Plating conditions</th>
<th>Thickness</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 g/L Pd(NH₃)₂Cl₂, 75 g/L NH₄Cl</td>
<td>SRR99</td>
<td>pH of 8</td>
<td>—</td>
<td>62</td>
</tr>
<tr>
<td>20–30 g/L Pd(NH₃)₂Cl₂, 40–60 mL/L NH₃ · H₂O, and 15–25 g/L NH₄Cl</td>
<td>M38</td>
<td>pH of 9–9.5, 15–50°C and 4–6 mA dm⁻²</td>
<td>8 μm</td>
<td>63</td>
</tr>
<tr>
<td>PdCl₂ 10 g cm⁻³, H₂NSO₃ 100 g cm⁻³, HCl 20 g cm⁻³ and NH₄Cl 50 g cm⁻³</td>
<td>713LC</td>
<td>At 35°C</td>
<td>3–7 μm</td>
<td>18 and 64</td>
</tr>
<tr>
<td>Solution comprising Pd(NH₃)Cl₂</td>
<td>Inconel-738LC</td>
<td>Current density of 3 A dm⁻² for 3 min</td>
<td>2–4 μm</td>
<td>7</td>
</tr>
</tbody>
</table>

6. **Ir, Re and Rh Electrodeposition**

IrBr₃ is generally reported as the most useful starting material for iridium deposition, as good deposits can be obtained from these electrolytes at a current density of 0.1–0.2 A dm⁻², pH around 1.8 with current efficiency of 30–65%. A pure Ir layer was electrodeposited on the nickel-based single crystal superalloy TMS-75. The basic electrolyte used for the pure Ir electrodeposition is composed of 4–12 g/L IrCl₃ · 4H₂O and 35–50 g/L HOSO₂NH₂. The electrodeposition was conducted at temperature of 353 K and pH value 2.0 with 0.1 μm/min rate. Iridium-modified aluminide coatings show reasonable cyclic thermal oxidation probably because of Ir presence in the coating, which not only improves the adherence of oxide scale but also delays the degradation of β-(Ir, Ni)Al phase to the γ’-phase during oxidation. Some researchers reported that addition of Ir to aluminide improves the protective performance of the aluminides by increasing the surface concentration of Al to approximately 70 at. % and retarding the interdiffusion of the alloying elements. Ir–Pt alloy has been successfully electroplated on an Ni-based single crystal superalloy TMS-75 by Murakami et al. The electrolytes were prepared from amidosulfuric acid (HOSO₂NH₂: 38–48 g/L), iridium chloride (IrCl₃ · 4H₂O: 40 g/L) and chloroplatinic acid hexahydrate (H₂PtCl₆ · 6H₂O: 55.5 g/L), where sodium nitrate (NaNO₃: 40–50 g/L) was added to improve their conductivity. The bath pH was adjusted using 2 N HCl or 1 N NaOH and the cathodic current density was set as 0.5–4.0 A dm⁻². In connection with oxidation test results of Ir–Pt-modified aluminide coatings, authors reported that these coatings are promising for replacing the conventional Pt–Al ones because Ir may...
play a role as solid solution strengtheners and does not deteriorate the creep properties of substrates.67

Re electrodeposition was also carried out by some authors on Ni-based superalloys K3,61 TMS-8268 and Hastelloy X. In another study,69 MCNG Ni-based superalloy substrate was coated by electrolytic Re using a solution comprising Rh2(SO4)3 at room temperature with a current density of 3 Adm−2 for 5 min. The thickness of the Rh layer was reported approximately as 2–3 μm, where the coatings have good adherence to the substrate without any blisters and pores. They used Re deposits for modification of aluminide coating. Based on XRD and EPMA analyses, after oxidation tests of Rh-modified aluminide, Bai et al. found that a continuous thin oxide scale of compact Al2O3 was formed at the surface of Rh–Al specimen and adhered to the substrate after the cyclic oxidation test. This oxide layer indicated no cracks and it effectively prevented the substrate from oxidation under the unfavorable condition of cyclic thermal stresses. Moreover, it was reported the Rh remains within the oxide scale and substrate serves as a barrier against the outward depletion of aluminum atoms in the cyclic oxidation process.7

7. Ni and Ni Alloy Electrodeposition

Although electrodeposition of nickel is very common, there are few reports related to electrodeposition of nickel on superalloys substrates. Nickel with 2 μm thickness was electrochemically plated from sulfate-chloride electrolyte on superalloy M38. An electrolyte consisting of 250–300 gl−1 NiSO4⋅7H2O, 30–60 gl−1 NiCl2⋅6H2O, 35–40 gl−1 H3BO3 (the famous Watts solution) with respective pH, temperature, and cathodic current density of 3–4, 45–60°C, and 1–2.5 Adm−2 were used as well as a nickel sheet for anode material. Narita et al. electroplated pure 5 μm thick Ni from Watts solution at a temperature of 70°C on TMS-82t and Hastelloy X. Before electrodeposition, they ground the specimens with 150-grit water-proof sand paper, followed by degreasing them in a methanol–benzene solution under ultrasonic agitation.68 In another research, Watts nickel bath (NiSO4⋅6H2O: 0.95 molL−1; NiCl2⋅6H2O: 0.17 molL−1; H3BO3: 0.65 molL−1) was used for Ni electrodeposition on superalloy TMS-82t.68 Some researchers70 plated Ni on Inconel-718SPF using electroless process. Since electroless nickel plating is an autocatalytic reaction process, the nickel ions (Ni2+) existing in a nickel electroless bath react with hypophosphorus ions (H2PO2−) to form nickel atoms. Meanwhile, the hypophosphorus ions react with nascent hydrogen to form phosphorus atoms. The nominal reaction is

\[ \text{Ni}^{2+} + \text{H}_2\text{PO}_2^- \rightarrow \text{Ni} + 2\text{H}^+ + \text{H}_2\text{PO}_3^- . \]

Electrodeposition of Pd–Ni was successfully carried out using an electrolyte comprising 15–45 gl−1 Pd(NH3)2Cl2, 30–50 gl−1 NiSO4⋅7H2O, 70–100 mL−1 NH3⋅H2O and 40–60 gl−1 NH4Cl.68 In addition, Pd–20%Ni coating was applied on superalloy M38 with plating conditions at pH 8.5–9, temperature of 15–50°C and 0.8–1.2 Adm−2. Narita and coworkers also used Pt as an anode material, where they electroplated a 10 μm-thick Re–Ni alloy film containing approximately 70 at.% Re from a pH of 3 aqueous solution using an Ni anode at a temperature of 50°C. The solution contained ReO4− (0.1 molL−1), nickel sulfate (0.1 molL−1) and citric acid (0.1 molL−1). They used TMS-82t and Haselloy X in their research as substrates.

Cavaletti et al.71 electrodeposited Ni–W coatings as a diffusion barrier to limit interdiffusion between an Ni-based superalloy MCNG and a β-NiAl bond coat. Ni–W coatings were plated from an electrolytic bath containing 20 gl−1 NiSO4⋅7H2O, 100 gl−1 NaWO4⋅2H2O and 66 gl−1 C6H6O7⋅H2O. The respective pH, temperature and current density of the bath were fixed at 7.5 and 70°C and 15 Adm−2. Authors reported preparation of 7 μm-thick Ni–W coating with a composition of Ni (75–80 at.%) and W (20–25 at.%) through 10 min deposition. Along with electrodeposition of Ni–W on superalloy substrate, they reported that W-rich layer formed with Ni–W coating modifies the oxidation behavior of the bond coat and limits inter-diffusion of substrate alloying elements. In another work Mercier et al.69 electroplated 7 μm-thick Ni–W electrolytic layer on as
Rhenium-deposited Ni-based superalloy (MCNG) from above mentioned electrolytic bath. Regarding the obtained coating some authors reported that the combination of Re and Ni–W electrolytic deposits demonstrates satisfactory thermal characteristics.

8. Composite Electrodeposition

Ouyang et al.\textsuperscript{72} electrodeposited Ni–BaCr\textsubscript{2}O\textsubscript{4} composite coatings (Fig. 6) on superalloy Inconel-718 from a Watts-type electrolyte containing BaCr\textsubscript{2}O\textsubscript{4} particles, dispersed in suspension with the aid of a cationic surfactant cetyltrimethylammonium bromide (CTAB). They reported the optimum electrodeposition parameters as 70 g\textsuperscript{-1} of BaCr\textsubscript{2}O\textsubscript{4} powder concentration in solution, temperature of 50°C and 2 A\textsuperscript{m}\textsuperscript{-2} of current density, where CTAB used as additive in the electrolyte was with a concentration of 0.05 g\textsuperscript{-1}. The BaCr\textsubscript{2}O\textsubscript{4} content in composite coating was reported as 16.6 vol.% under optimum electrodepositing condition. This composite coating exhibited a relatively smooth surface and uniform distribution of BaCr\textsubscript{2}O\textsubscript{4} particles. The authors demonstrated that the content of BaCr\textsubscript{2}O\textsubscript{4} incorporated into composite coatings depends mainly upon the BaCr\textsubscript{2}O\textsubscript{4} powder concentration in bath, cathode current density and temperature of electrolyte. They also investigated the friction and wear properties of Ni–BaCr\textsubscript{2}O\textsubscript{4} composite coatings with a ball-on-disk friction and wear tester in sliding against alumina ball. Their results showed that the wear resistance of Ni–BaCr\textsubscript{2}O\textsubscript{4} composite coating electrodeposited on superalloy Inconel-718 increases with increasing the BaCr\textsubscript{2}O\textsubscript{4} content.

Since electrodeposition of MCrAlY coatings is a new attempt involving easy and cost-effective application of overlay or bond coatings on the hot section parts of gas turbines, NiCrAlY coating was applied to nickel-based superalloy Inconel-738 using electrolytic deposition by Saremi and Bahraini.\textsuperscript{19} Before plating, the samples were treated anodically in concentrated (65–70\%) H\textsubscript{2}SO\textsubscript{4} at room temperature and at 20 A\textsuperscript{cm}\textsuperscript{-2} for 1 min based on ASTM B558. To obtain NiCrAlY coating, nickel was electroplated using a Watts bath containing aluminum (5 g\textsuperscript{-1}) and chromium (25 g\textsuperscript{-1}) particles, where yttrium was applied by hot-doping. The electrodeposition parameters for NiCrAl deposition were the current density of 5–7 A\textsuperscript{m}\textsuperscript{-2}, temperature of 50–65°C, pH of 4 and plating time of 20–30 min. Here, heat treatment was also used to homogenize the coating. It was reported that all four elements are present in the coatings within the desired concentration range, as well as two phases of α-Cr and β-NiAl. The hot corrosion resistance of the coating was studied by an electrochemical test method, where a notable performance of such a coating at high anodic polarization was observed. As the adhesion of the coating during 100 h of cyclic oxidation was acceptable, the hot corrosion and oxidation resistance consequently show a significant improvement. Electrodeposition of Ni(Zr) composite coating on Cr-pack-cemented Ni-based superalloy TMS-82t was also reported elsewhere.\textsuperscript{68} Ni(Zr) film was coated using an Ni Watts solution containing 6 g\textsuperscript{-1} Zr powder solution, under a current density of 1.5 A\textsuperscript{m}\textsuperscript{-2}, where the average size of the Zr powder was 3 μm. The Ni(Zr) composite electroplated specimen was heat treated in the temperature range of

![Fig. 6. Surface morphologies of pure nickel coating and Ni–16.60 vol.% BaCr\textsubscript{2}O\textsubscript{4} composite coating: (a) Pure nickel coating; and (b) Ni–16.60 vol.% BaCr\textsubscript{2}O\textsubscript{4} composite coating. Source: Reprinted with permission from Ouyang et al.\textsuperscript{72} Copyright: Elsevier (2013).]
800–1150°C in a vacuum of 10–3 Pa to allow Zr becoming evenly distributed in the composite coating.

An Ni-based composite plating bath was patented by Grossman and Grylls. Their invention provided a method to coat the superalloy substrate using a plating process, either electroless or electrolytic, whereby Ni, Co, Fe or combinations thereof (but preferably Ni) was plated on the superalloy substrate using a solution that included a suspension of powders or containing one or more of the following elements: Ni, Cr, Al, Zr, Hf, Ti, Ta, Si, Ca, Fe, Y and Ga. It was also reported in their invention that the optional heat treatment at a temperature above 870°C and time between 30 min and 150 min are sufficient to allow diffusion between the elements comprising the entrapped powders and the matrix.

9. Concluding Remarks

Electrodeposition of metals, alloys and composites on superalloy substrates was successfully carried out to improve and modify the oxidation and hot corrosion behavior of high-temperature coatings applied widely on gas-turbine engine components. These electrodeposited films are usually deposited in the range of 2–7 μm thickness. The important factor in almost all of these electroplated coatings is the diffusion treatment. Applying diffusion treatment to the coatings provides their good adherence to the superalloys.

Since superalloys are passivated by the formation of surface oxide films, which reduces adhesion of plated films, special cleaning and processing are required to remove these films prior to electrodeposition.

To stabilize β-phase and delay transformation of β-phase to γ′-phase, platinum and its alloys were electroplated before aluminizing. P- and Q-electrolyte are used extensively for electrodeposition of Pt on superalloys. Platinum and layered structures of Pd, Ir, Ru and Re were electrodeposited on different superalloys. Nickel and nickel alloys were also plated using either electrodeposition or electroless methods. The well-known Watts bath was utilized for nickel plating. Furthermore, NiCrAlY, Ni–BaCrO₄ and Ni(Zr) coatings were applied as composite coatings on Ni-based superalloys.

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