THE PERFORMANCE OF Pt-MODIFIED ALUMINA-FORMING COATINGS AND MODEL ALLOYS

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Abstract

The oxidation behavior of two-phase, γ+γ' Pt diffusion coatings and model alloys has been evaluated to better understand the potential of this class of coatings for power generation applications. Coatings were deposited on both directionally-solidified alloy 142 and single crystal N5 superalloys. Fabrication issues such as initial Pt thickness and annealing temperature were evaluated. Oxidation testing was performed in both dry O2 and with the addition of H2O to study the performance of γ+γ' and conventional coating materials. After exposure for 1000, 1-h cycles at 1150°C in dry O2, a γ+γ' coating on N5 had evolved into a thicker, almost continuous γ' layer with the Pt content dropping to ~7 at.% in this layer and diffusing ~250µm into the substrate, disrupting the γ+γ' substrate microstructure. Characterization of the oxide formed on a γ+γ' composition showed that even 30 at.%Pt did not prevent the formation of a Ni-rich spinel layer at 1200°C. In order to assist the coating development process, model alloys also were evaluated. Other Pt group metals (Pd and Ir) were evaluated as well as the addition of Cr and various Hf levels. As expected, Cr and Hf were beneficial for oxidation resistance. However, Pd was not an adequate replacement for Pt because of the multi-phase microstructure that formed. A γ+γ' composition had a 1000°C yield stress in compression that was significantly higher than γ'-Ni3Al or β-NiAl. Also, the thermal expansion coefficient was very similar to other Ni-Al alumina-formers. The performance of γ+γ' compositions are very promising, however, sensitivity to superalloy substrate composition, Pt interdiffusion during long-term service, spinel formation and the potential need for a secondary processing step are areas of concern for this class of coatings.

Introduction

There has been significant recent interest in the use of two-phase, γ (Ni-solid solution) and γ'(Ni3Al) bond coatings (sometimes called Pt diffusion coatings or low-cost bond coats) for thermal barrier coatings (TBC’s) on superalloys because of their combination of oxidation resistance, good mechanical properties, limited Al interdiffusion behavior and lower cost.[1-9] However, limited information is available about their fabrication, performance and limitations. The current study is being conducted to evaluate the potential of this class of coatings for next generation power generation applications where long-term durability and improved corrosion resistance are issues. The burning of synthetic gas from coal in turbines will increase the water vapor content in the combustion gas[10] and may bring higher levels of other impurities, such as sulfur, than current natural-gas fired turbines. Coatings based on γ+γ' compositions may be attractive for this application because they are reported to have lower Al interdiffusion[2], which may result in increased lifetime, and good hot corrosion resistance.[5]

Like aero-turbines, the current generation of land-based turbines relies on TBC’s to protect hot section components. Lifetime of TBCs has been related to the adhesion of the alumina scale that forms at the interface between the metallic bond coating and the low thermal conductivity, ceramic (typically Y2O3-stabilized ZrO2(YSZ)) top coat.[11-12] The scale is a weak link that must be almost ideally adherent to retain the top coat. Therefore, characterizing the formation, growth and adhesion of this oxide layer is an initial method for assessing the potential of this class of materials as bond coatings. Coatings on superalloy substrates and model coating alloys have been evaluated in furnace cycling tests in dry O2 and in air with 10-90 vol.%H2O. Using model alloys allowed evaluation of possible modifications in coating composition for improved performance or due to compositional changes during service. Also, because oxidation resistance is not the only factor that governs coating performance, an initial assessment was made of the thermal expansion behavior and the high temperature yield strength of a γ+γ' alloy relative to other aluminate compositions. The current assessment is that γ+γ' coatings have some attractive features including oxidation resistance and mechanical properties. Concerns about Pt interdiffusion in the substrate, the formation of Ni-rich spinel oxide, sensitivity to superalloy composition and the need for secondary processing steps are discussed in this paper.

Experimental Procedure

The model alloys were vacuum induction melted at Oak Ridge National Laboratory (ORNL) using a water-chilled copper mold. Chemical compositions were measured by inductively-coupled plasma analysis and combustion analysis on as-cast material, Table I. All compositions in the paper are in atomic percent. After casting, alloys were annealed for 4h at 1300°C in quartz ampules or at 104Pa (10 -6Torr) vacuum except for Ni-5Pt-9Cr-22Al which melted at <1300°C and was annealed at 1200°C. Oxidation coupons (1-1.5mm thick, typically 15mm diameter) were polished to a 0.3µm alumina finish and cleaned in acetone and methanol prior to oxidation.

Two types of General Electric Aircraft Engines superalloy substrates were coated, directionally-solidified (DS) alloy 142 (PCC Airfoils) and single crystal (SX) alloy N5 (Howmet), Table I. The substrates were first grit-blasted (alumina) and then
electroplated with ~7 or 12µm of Pt in a laboratory scale bath at Tennessee Technological University (TTU). The coatings were then annealed for 2h at 1100° or 1175°C in a vacuum of 10⁻⁴ Pa (10⁻⁶ Torr).

Two types of cyclic oxidation experiments were conducted: (1) 500h cycles in laboratory air at 1000°C in a box furnace with specimens in individual, pre-annealed alumina crucibles which captured any spalled oxide[13]; or (2) an automated test rig, where the specimens were hung by Pt-Rh wire and cycled for 1h at 1100° or 1150°C and 10min cooling in dry, flowing O₂ or in air with 10⁻⁹vol.% H₂O. For the wet air tests at 1100°C, a controlled quantity of distilled water was atomized into the gas stream above its condensation temperature. Specimen mass change was measured using a Mettler-Toledo model AG245 balance.

After oxidation, specimen characterization included a field emission gun, scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectrometer (EDS); and electron probe microanalysis (EPMA) using wavelength dispersive x-ray analysis. Specimens were Cu-coated before being sectioned for metallography. A scanning transmission electron microscope (STEM) equipped with EDS was used to analyze cross-sectional specimens fabricated by focused ion beam (FIB) milling[14]. During FIB specimen preparation, a W layer was deposited to protect the gas interface of the scale.

**Results**

**Coating Fabrication**

Because there are few details in the literature about the fabrication procedure for γγ' coatings, it is difficult to know if there is an optimal process or if a two stage process is needed. The second stage could be a pack or CVD process to increase the Al, Cr, Hf, etc. content of the coating after Pt-plating[5,7,15,16]. The first γγ coatings[3,4,9,15] made at ORNL/TTU used ~7µm Pt, the same amount as in conventional low activity chemical vapor deposition aluminide coatings[17], and a 2h vacuum anneal at 1150° or 1175°C. However, these coatings generally showed inferior oxidation resistance to conventional Pt-modified aluminide coatings on the same substrates[4,9,15].

Based on open literature and patent information,[7,18-20] two parameters were selected for evaluation: Pt thickness and annealing temperature[21]. Figure 1 shows the effect of Pt thickness on the coating Pt and Al contents. Obviously the Pt content was higher when 12µm of Pt was deposited. Due to Pt lowering the activity of Al,[2,22] the coating became enriched in Al and slightly depleted the adjacent substrate in Al compared to the average N5 substrate content of 13.9%Al, Table I. Somewhat surprisingly, the Al content was slightly lower with the higher Pt content, Figure 1. However, the Ni content was lower in the coating with more Pt.

Varying the annealing temperature between 1100° and 1175°C had a minor effect on the coating content.[21] The biggest difference was a higher Al content with the higher annealing temperature. In recent cyclic oxidation tests, the performance of coatings with 12µm Pt and a 2h 1175°C anneal have been compared to coatings with a 7µm Pt layer.

**Cyclic Oxidation Performance of Coatings**

Figures 2 and 3 show some of the cyclic oxidation mass gain results for the γγ' coatings with an initial Pt thickness of 7 or 12µm.[21] In both cases, the mass change for a specimen of NiAl+Hf is shown as a baseline, adherent alumina-former. At
1100°C, increasing the Pt content reduced the mass gain for $\gamma+\gamma'$ coated alloy 142. With only 7µm of Pt, a significant amount of Hf internal oxidation occurred, Figure 4a, for this DS alloy with 0.52Hf, Table I. In model alloys, increasing the Pt content decreased the amount of Hf internal oxidation.[6,23] Therefore, the lower mass gain observed for the coating on 142 with the higher Pt content, Figure 2, was attributed to a reduction in Hf internal oxidation. This specimen has not yet been characterized to confirm this hypothesis. At 1150°C, the 7µm Pt $\gamma+\gamma'$ coating on alloy 142 performed very poorly with significant spallation in less than 100 cycles on two different specimens, Figure 3. Increasing the Pt content decreased the initial mass gain, but the subsequent mass gain was higher than for coated N5 as Ni-rich oxide nodules began to form after 200 cycles. On a high Hf content DS superalloy such as alloy 142, $\gamma+\gamma'$ coatings may not be appropriate for such high temperature applications.

For N5 substrates with only 0.04Hf, $\gamma+\gamma'$ coatings with only a 7µm Pt layer have shown excellent cyclic oxidation resistance, with a relatively low mass gain at 1100°C and little indication of scale spallation after >1,500 cycles, Figure 2. (This particular N5 variation contains Y, Table I, the performance of other variations...
without Y are reported elsewhere.[9,21] At 1150°C, the γ+γ' coating on N5 with 12µm Pt did not show any signs of spallation after 400 cycles, Figure 3. However, with a 7µm Pt coating, small amounts of scale spallation were observed after ~600 cycles, corresponding to the small mass losses, Figure 3. Similar scale spallation was not observed for conventional Pt-modified aluminide coatings on this substrate at this temperature.[9] After 1,000 cycles, the 7µm N5 coating specimen was sectioned and characterized. Figure 4b shows the ~5µm alumina scale formed on the coated substrate with virtually no internal oxidation. The second phase precipitates forming a line in the coating contained Al and O and are likely remnants from the grit blasting. Figure 5 is an SEM image of the same coating to show the γ+γ' microstructure. There appears to be a γ layer adjacent to the surface oxide followed by an almost a complete layer of γ'. Underneath the coating, an extensive γ' depletion zone is shown in the N5 substrate. An EPMA line profile in Figure 6 shows the concentration of Pt and Al to a depth of 240µm where the Pt content had dropped to <0.5% after the 1,000h exposure at 1150°C. Compared to the original coating composition, also shown in Figure 6, a significant amount of Pt and Al interdiffusion had occurred. The ~5µm surface γ layer contained only ~5%Pt and <11%Al. The underlying γ' layer with ~19%Al and 7%Pt was significantly thicker than the original coating. Due to Al interdiffusion and Al consumption via oxidation (and spallation), a significant drop in the adjacent substrate Al content had occurred, Figure 6, to at least 200µm. Characterization of the 12µm Pt coating after 1,000 cycles is needed to determine if a higher Pt content affects this interdiffusion behavior.

Effect of H2O on Oxidation Behavior

Because of the higher water vapor contents in the combustion environment with the use of coal-derived synthetic gas, the oxidation performance of γ+γ' coatings also was investigated in higher water vapor contents than the typical 10-15%H2O found with burning natural gas.[10,24] Figure 7a shows the mass gain behavior of 7µm Pt γ+γ' coatings on N5 substrates at 0, 50 and 90vol.% H2O. The mass change was very similar to the baseline

To put these γ+γ' coating results into perspective, Figure 9 shows the mass gain of two model bond coating alloys as a function of water vapor content during cyclic oxidation at 1100°C. For Ni-48Al+Hf, the addition of water vapor caused a small increase in the mass gain with increasing water vapor content. The gas interface of the α-Al2O3 scale showed signs of evaporation under these conditions.[24] This is consistent with a low level of reaction to form a volatile Al-OH type compound at this temperature.[29]
For cast NiCrAlYHf, representative of MCrAlY-type coatings, the effect of water vapor was to slightly increase the scale spallation with the higher water vapor contents. The scale spallation for NiCrAlYHf is attributed to the faster scale growth (higher mass gain) compared to NiAl+Hf and the higher coefficient of thermal expansion (CTE)\[30\], which increases the thermal stresses between the metal and alumina scale (see data in Fig. 18).

**Model \(\gamma\gamma'\) Alloy Oxidation Behavior**

As with the model NiCrAlYHf and NiAl+Hf alloys, model alloys also have been used to study the oxidation behavior in the \(\gamma\gamma'\) system.[2,3,5-7] Because of the transient oxide formation and the interdiffusion observed in \(\gamma\gamma'\) coatings, the primary interest for this study[23] was on the oxidation behavior of \(\gamma\gamma'\) alloys with relatively low Pt contents, e.g. 5-10%, that would help to understand the behavior of mature coatings. Also, to study the transient behavior of these materials, the temperature was reduced to 1000°C, closer to actual coating application temperatures, especially in land-based turbines. (Higher temperature testing, i.e. 1100°-1200°C, should favor the formation of \(\alpha-Al_2O_3\) because of the faster Al diffusion in the substrate and avoid the possible formation of metastable cubic alumina phases such as \(\theta-Al_2O_3\).[31,32]) Figure 10 shows the effect of platinum group metal (PGM) additions (Pt, Pd, Ir) and Hf on the mass gain after 500h at 1000°C in air. As a (dashed) baseline, Ni-48Al+0.05Hf sets a minimum in terms of no Ni-rich oxide formation, minimal Hf internal oxidation and slow alumina growth. The Ni-22Al alloys with no PGM addition showed higher mass gains, primarily due to the transient formation of Ni-rich oxides. (With 4000ppm Hf, internal oxidation of Hf also added to the mass gain.) With modest (200-700ppm) Hf additions, increasing Pt additions reduced the amount of transient oxide and thus the mass gain decreased. For example, Figure 11a shows the thick Ni-rich oxide formed with only 5Pt. Alloys with no Hf or 4000ppm Hf showed a similar trend. However, there was an unusual change with increasing Pt content with 4000ppm Hf. With 5Pt, the mass gain...
was a combination of internal Hf oxidation, Fig. 11b, and Ni-rich oxide, indicated by the faceted gas interface in Fig. 12a. With 10%Pt and high Hf, the mass change was similar but the internal oxidation was eliminated, Fig. 11c, due to the proposed interaction between Pt and Hf.[6,7] However, the gas interface was irregular due to the faster growth of \( \theta \)-\( \text{Al}_2\text{O}_3 \) with its hallmark[31,32] blade-like morphology, Fig. 12b. The metal-oxide interface, Figure 11c, also was irregular because the \( \theta \)- to \( \alpha \)-\( \text{Al}_2\text{O}_3 \) phase transformation occurs non-uniformly.[32] Thus, these variations in composition resulted in complex changes in the oxidation behavior.

The issue of replacing Pt with another PGM also was explored. Both Pt and Ir showed a similar benefit at the 5% level, Figure 10. Higher levels of Pd, which is significantly less expensive than Pt, were less effective due to the formation of additional alloy phases, Figure 13. Higher Pd levels also resulted in a lower melting (solidus) temperature, <1300°C.[3] The co-addition of 5%Cr and ~10%Pt did not decrease the mass gain but, the addition of both ~700ppm Y and 700ppm Hf resulted in additional internal oxidation, Figure 11d, that increased the mass gain in this specimen, Figure 10. A Ni-22Al-10Cr-5Pt specimen showed a lower mass gain but also a lower solidus temperature, <1300°C. Also, these levels of Al and Cr are almost high enough to eliminate transient oxide formation without a PGM addition.[33] In addition to improving the selective oxidation of Al,[34] another reason for adding Cr was to increase the hot corrosion resistance.[5] In general, these results suggest that >10%Pt is needed to prevent significant Ni-rich oxide scale formation.

The formation of transient, Ni-rich oxides was further studied because these oxides are linked to TBC failure[35,36] and the \( \text{Al}_2\text{O}_3 \)-NiAl\(_2\)O\(_4\) interface is thought to be weak because of observations of interfacial voids.[37,38] However, because of the
thin oxide layers formed on these alloys, characterization by SEM, EPMA or x-ray diffraction was difficult. The surface morphology was a good indicator, such as in Figure 12. Figure 14a shows the typical $\alpha$-Al$_2$O$_3$ morphology on $\beta$-NiAl+Hf after oxidation at 1200°C for 2h. However, even with 30Pt, $\gamma+\gamma'$ compositions without Cr tended to show different surface morphologies, Figure 14b. To confirm the presence of a Ni-rich surface oxide, a TEM cross-section was made. Figure 15 shows the scale formed on Ni-22Al-30Pt-0.02Hf after 2h at 1200°C. As in Figure 11c, the metal-oxide interface is irregular, likely due to local variations in the phase transformation to the slower-growing $\alpha$-Al$_2$O$_3$ phase. Above the $\alpha$-Al$_2$O$_3$ layer is a distinct NiAl$_2$O$_4$ oxide layer. In this case, the Al$_2$O$_3$-NiAl$_2$O$_4$ interface appeared to be void free, similar to the observation for Ni-35Al+Hf.[3] Because of the underlying alumina layer, the NiAl$_2$O$_4$ likely would not grow further but could inhibit the bonding between the alumina scale and the ceramic top coat in a TBC system.

Mechanical and Physical Property Measurements

Finally, the high temperature yield stress and CTE were measured to obtain some additional information relevant to $\gamma+\gamma'$ coatings. One of the reported[8] attractive features of $\gamma+\gamma'$ coatings is good mechanical properties, yet no information has been provided in the open literature. As a first assessment of the high-temperature mechanical properties, compression yield tests were conducted on several Ni-Al alloys at 1000°C with a $10^{-3}$s$^{-1}$ strain rate. (Additional details of the experimental procedure are available elsewhere.[39]) Figure 16 compares the 0.2% engineering yield stress of N5, Ni-22Al-10Pt-0.05Hf, Ni-25Al+0.05Hf, Ni-48Al+Hf and NiCoCrAlY, Table I. The yield stress of the $\gamma+\gamma'$ composition was similar to N5 and significantly higher than NiAl or MCrAlY.

Figure 17 shows the mean CTE for Ni-22Al-5Pt-0.02Hf as a function of temperature compared to other Ni-base materials.[23,30] (Experimental details are available elsewhere.[30]) The CTE was remarkably similar to $\beta$-NiAl at 1000°-1200°C and showed no indications of a phase transformation, as in NiCoCrAlY or Ni-35Al.

Discussion

Because of the proprietary nature of bond coating development, particularly for these new $\gamma+\gamma'$ coatings, there is little information
available in the literature on which to base an assessment. Therefore, an experimental program on coatings and model alloys has been conducted. The absence of coating fabrication details places the coating work at a particular disadvantage because of the many process variables, particularly for a secondary treatment. However, if γ+γ' coatings are to be “low cost” bond coatings (LCBC), the simple processing route reported here is necessary. In that case, two of the main variables are Pt thickness and annealing temperature and those are currently being assessed.[21]

For the model alloy work, the effects of Pt, Al and Hf observed here appeared to be consistent with the literature.[2,3,5-7,22,40-44] One exception was the transient θ-Al2O3 formation observed at 1000°C on Ni-22Al-10Pt-0.4Pt which had not been discussed previously. The model alloy work on Pd and Ir did not appear to be a promising route for coating development. However, another study[44] suggested that a mixture of Pt and Hf did not appear to be superior to conventional aluminides.[5] The oxidation resistance, particularly with the addition of Hf, appears to be superior to conventional Pt-modified and MCrAlY coatings. One advantage of the γ+γ' compositions is higher Hf solubility, which increases the processing window for Hf doping.[2] Prior efforts to dope conventional aluminide coatings with reactive elements such as Hf[45] have not been commercially successful. The optimal Hf content in γ+γ' coatings appears to be a function of the Pt content.[6] For example, Figures 11b and 11c show the suppression of Hf internal oxidation by increasing the Pt content. This is an issue for the substrate Hf content as well. Higher Hf content substrates appear to need higher Pt content γ+γ' coatings to suppress internal Hf oxidation, Figure 4a. However, one difference between the 142 and N5 substrates is the higher S content in the former, Table 1, which may have negatively impacted their oxidation performance.[46]

Some of the other attractive features of γ+γ' coatings are mechanical strength and CTE. The higher strength should limit fatigue problems. Of course, much more work is needed to understand the mechanical properties in this system. The relatively low CTE measured (Fig. 17) likely explains the good scale adhesion in this system. The thermal stress that drives scale spallation is a function of the CTE mismatch between the metal and scale.[47]

There are several concerns about these coatings:
(1) Substrate compatibility: Based on the results with 142 and N5 substrates, γ+γ' coatings are sensitive to the superalloy substrate composition, which is true to some degree for all bond coatings. However, aluminide coatings have lower solubility for many substrate elements, making them less sensitive than γ+γ' coatings. Thus, γ+γ' coatings may not be suitable for certain superalloy compositions and conditions.

(2) Pt interdiffusion: Initially it was hoped that these coatings offered higher temperature capability than other coatings. However, based on the Pt interdiffusion observed, Figure 6, this appears somewhat unlikely.[8] Although the Al content does not decrease significantly, as it does for β and MCrAlY coatings, the loss of Pt is an issue for retaining the oxidation resistance with such a low Al content. An additional concern is the disruption of the substrate γ+γ' microstructure, which could reduce the superalloy creep strength. Particularly for thin-walled airfoils, this may be a concern that needs to be further evaluated.

(3) Ni-rich spinel oxide formation: The transient formation of Ni-rich oxides may be a concern for TBC processing where a strong Al2O3-YSZ bond is desired. Initially oxidizing with low O2 partial pressures can suppress the formation of Ni-rich oxides by making them thermodynamically unstable.[48] However, in service spinel
formation, particularly in the presence of water vapor, could reduce the TBC lifetime. When the scale reaches a critical thickness, spallation is observed for all alumina-forming alloys. Figure 18 shows schematically a wedge-type failure.[47] For a typical alumina-forming substrate, the new oxide formed in the cracks would be alumina and the scale would heal to some degree. However, a spinel-forming substrate would fill the cracks with spinel, creating a permanent defect in the scale that would allow more rapid transport thereby increasing the scale growth rate and thus increasing the Al consumption rate. A similar model was proposed for the poor oxidation resistance of NiAl alloys.[38] Such a mechanism likely occurs for the failure of any Al-depleted, Ni-base alumina-forming coating, accounting for the formation of Ni-rich oxides at failure.[35,36] This mechanism could reduce the anticipated lifetime for these coatings.

(4) Secondary processing: Some of these concerns may be addressed by a secondary processing step where Al, Hf or other elements are added to a γ+γ′ coating. However, adding steps to the coating process will increase the cost and remove one of the attractive features of these coatings.

Summary

In order to assess the performance of γ+γ′ coatings for future power generation applications, γ+γ′ coatings and model alloys have been examined. Several factors affecting the fabrication and performance of coatings have been evaluated on N5 and 142 substrates. The performance of γ+γ′ coatings was much better on N5 substrates in both dry O₂ and with H₂O in the environment. This result needs to be further studied with different coating Pt contents and substrate S contents. Extensive Pt interdiffusion and substrate Al loss was observed after thermal cycling a γ+γ′ coating on N5 at 1150°C.

The oxidation performance of model γ+γ′ alloys also was examined. Replacing Pt with Pd or Ir did not appear to be promising. A Pt content of ~10% was needed to limit the amount of Ni-rich oxide formed at 1000°C. However, even with 30%Pt, a transient, Ni-rich oxide formed at 1200°C. The yield stress of a γ+γ′ alloy was significantly higher than β-NiAl or MCrAlY specimens. The thermal expansion was similar to other Ni-Al compositions.

The current assessment of γ+γ′ coatings is that they offer several attractive features including oxidation resistance and mechanical properties. Several concerns need to be addressed including the apparent sensitivity to superalloy composition, the effect of Pt interdiffusion in the substrate, the formation of Ni-rich spinel oxide, and the potential need for secondary processing steps.

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