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

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Abstract

The oxidation behavior of two-phase, + ' 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 O_2 and with the addition of H_2O to study the performance of + ' and conventional coating materials. After exposure for 1000, 1-h cycles at 1150°C in dry O_2, a + ' coating on N5 had evolved into a thicker, almost continuous ' layer with the Pt content dropping to ~7at.% in this layer and diffusing ~250μm into the substrate, disrupting the + ' substrate microstructure. Characterization of the oxide formed on a + ' composition showed that even 30at.%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 + ' composition had a 1000°C yield stress in compression that was significantly higher than '-Ni_3Al or -NiAl. Also, the thermal expansion coefficient was very similar to other Ni-Al alumina-formers. The performance of + ' 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, (Ni-solid solution) and '(Ni_3Al) 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 + ' 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 Y_2O_3-stabilized ZrO_2(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 O_2 and in air with 10-90vol.%H_2O. 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 + ' alloy relative to other aluminide compositions. The current assessment is that + ' 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 10^{-4}Pa (10^{-6}Torr) 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), TableI. The substrates were first grit-blasted (alumina) and then

	Ni	Al	Hf	Pt	Cr	C (ppma)	S (ppma)	Other
Ni-48Al+Hf	51.6	48.3	0.056		<0.01	340	<4	
Ni-51Al+Hf	48.8	51.1	0.050		<0.01	350	<4	
Ni-42.5Al+Hf	58.0	41.9	0.048		<0.01	380	<4	
Ni-25Al+Hf	75.1	24.8	0.057		<0.01	410	<4	
Ni-22Al-0.05Hf	76.9	22.8	0.049		0.01	770	<4	
Ni-22Al+0.5Hf	77.5	21.9	0.493		<0.01	130	<10	
Ni-22Al-5Pt	73.0	22.0	<0.01	4.9	<0.01	150	<10	
Ni-22Al-5Pt-0.02Hf	72.8	22.1	0.016	5.0	<0.01	240	<10	
Ni-22Al-5Pt-0.4Hf	72.8	21.8	0.403	4.9	<0.01	130	<4	
Ni-22Al-10Pt	67.8	22.2	<0.01	9.9	<0.01	270	<10	
Ni-22Al-10Pt-0.06Hf	67.0	22.6	0.062	10.2	0.01	110	<10	
Ni-22Al-10Pt-0.4Hf	68.1	21.7	0.393	9.7	0.01	120	<4	
Ni-22Al-15Pt-0.06Hf	62.2	22.5	0.061	15.1	0.01	180	<10	
Ni-22Al-30Pt-0.02Hf	48.0	22.1	0.021	29.5	0.19	80	<10	
Ni-22Al-5Pt-9Cr	63.5	21.4	0.074	4.8	10.0	230	<4	0.021 Y
Ni-22Al-10Pt-5Cr	63.2	21.4	0.070	10.2	5.0	150	<4	0.067 Y
Ni-22Al-5Ir+Hf	73.5	21.5	0.072		0.01	160	11	4.9 Ir
Ni-22Al-10Pd	66.1	23.9	0.078	<0.01	0.01	230	<4	9.8 Pd
Ni-22Al-20Pd	57.7	22.4	0.079	<0.01	0.01	200	<4	19.7 Pd
NiCrAlYHf	61.4	18.9	0.046		19.5	420	5	0.006 Y
MCrAlY	40.4	23.5	<0.01		17.4	420	8	18.5 Co, 0.15 Y
Alloy 142	59.5	13.9	0.520		7.8	6000	11	11.9Co,2.1Ta,1.5W 0.9Mo,0.9Re
Alloy N5	64.9	13.9	0.043		7.8	3180	4	7.3Co,2.1Ta,1.6W 0.9Mo,1Re,0.011Y

Table I. Chemical compositions of the cast alloys in atomic percent determined by induction coupled plasma and combustion analysis.

electroplated with ~7 or 12 μm 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 10⁻⁴Pa (10⁻⁶Torr).

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 O_2 or in air with 10-90vol.% H_2O. 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 + ' 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 + ' coatings[3,4,9,15] made at ORNL/TTUused ~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 + ' 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
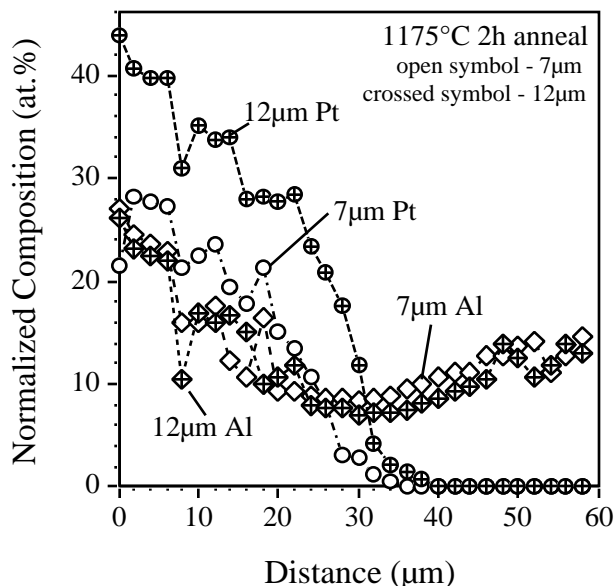
Figure 1. EPMA composition profiles from metallographically sectioned coatings with ~7 or 12μm of electroplated Pt on the surface of N5+Y after annealing for 2h at 1175°C.
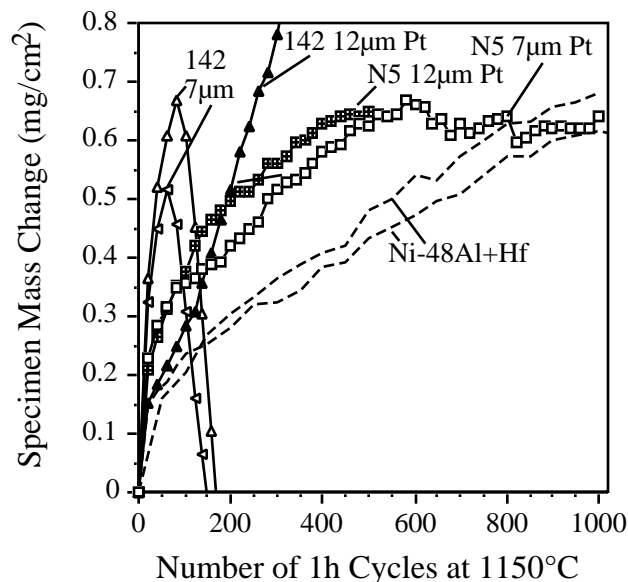

Figure 3. Specimen mass changes for + ' coatings on 142 and N5 substrates during 1h cycles at 1150°C in dry O_2.

1100°C, increasing the Pt content reduced the mass gain for + ' coated alloy 142. With only 7 μm 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 7 μm Pt + ' 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, + ' coatings may not be appropriate for such high temperature applications.

For N5 substrates with only 0.04 Hf, + ' coatings with only a 7 μm 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
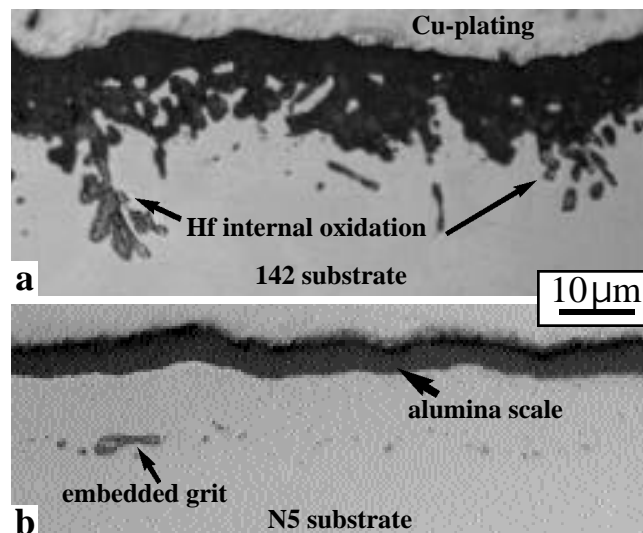

Figure 2. Specimen mass changes for + ' coatings on 142 and N5 substrates during 1h cycles at 1100°C in dry O_2.

Figure 4. Light microscopy of metallographic sections of the scale formed on a + ' (7 μm Pt) coating (a) on alloy 142 after 800, 1h cycles at 1100°C and (b) on alloy N5 after 1,000 1-h cycles at 1150°C.

without Y are reported elsewhere.[9,21]) At 1150°C, the + '
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 + '
microstructure. There appears to be a layer adjacent to the
surface oxide followed by an almost a complete layer of '.
Underneath the coating, an extensive ' 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 layer contained only ~5%Pt and
<11%Al. The underlying ' 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 H$_2$O 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 + ' coatings also was investigated in
higher water vapor contents than the typical 10-15%H$_2$O found
with burning natural gas.[10,24] Figure 7a shows the mass gain
behavior of 7μm Pt + ' coatings on N5 substrates at 0, 50 and
90vol.% H$_2$O. The mass change was very similar to the baseline
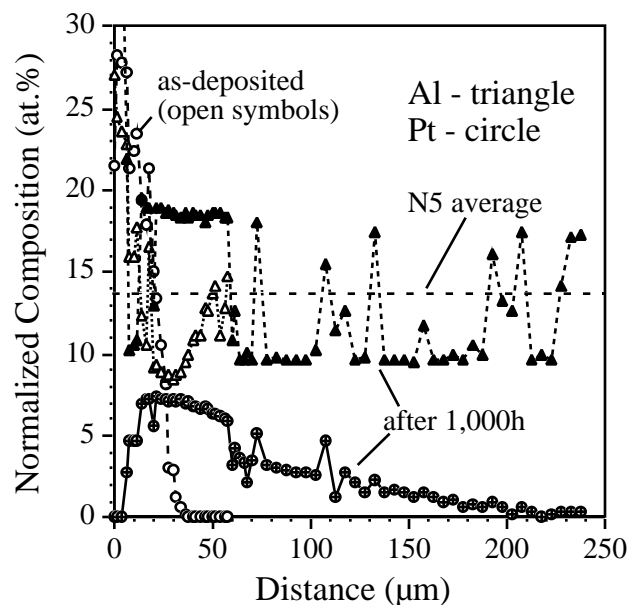
Figure 6. EPMA composition profiles from metallographically
sectioned coatings with ~7μm of electroplated Pt on the surface of
N5 as-annealed and after 1,000 1-h cycles at 1150°C. The dashed
line shows the average Al content for the N5 substrate.

NiAl+Hf that forms an adherent alumina scale (dashed line in
Figure 7a). Figure 7b shows the mass change for 7μm Pt + '
coatings on 142 substrates. These specimens were stopped prior to
1000 cycles because of excessive scale spallation and coating
degradation. Figure 8a shows scale spallation after exposure for
only 300, 1-h cycles in 50%H$_2$O. These results are consistent with
prior studies of water vapor effects.[25-28] Substrates such as
coated N5 that form adherent -Al$_2$O$_3$ scales tend to be less
affected by water vapor than those that form less adherent scales,
such as on 142.

Besides the spallation for the coated 142 specimens, which may be
due to the lower than optimal Pt (7μm) content, the other concern
about these results is the increased mass gain with the addition of
water vapor, Figure 7b. A similar increase was noted for a model
Ni-22Al-10Pt-0.4Hf alloy which has a high Hf content like the 142
substrate, Table I. The increase in mass gain was attributed to
increased formation of Ni-rich, spinel type oxide, such as NiAl$_2$O$_4$.
Figure 8b shows the scale formed on coated 142 after 200, 1-h
cycles in air+90%H$_2$O. The triangular features (arrows) are the
hallmark of a cubic Ni-rich oxide, like NiAl$_2$O$_4$. Increased
transient oxide formation also has been reported in previous
studies of the role of water vapor.[27-28]

To put these + ' 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 -Al$_2$O$_3$ 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]

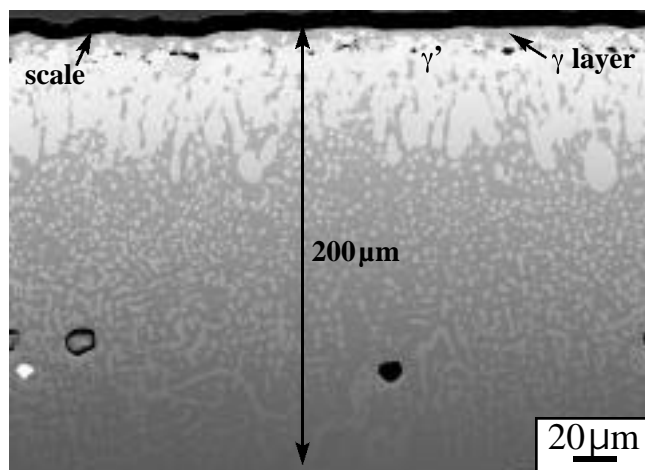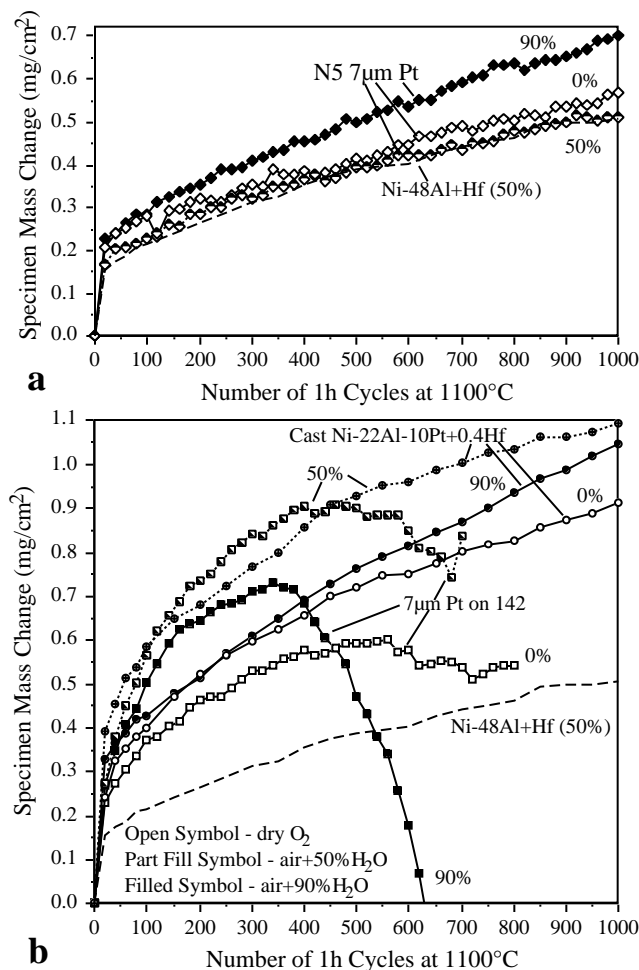Figure 5. SEM secondary electron image of a polished section of
the 7μm Pt coating on N5 after oxidation at 1150°C for 1,000, 1-
h cycles in dry O$_2$. The ' layer is rich in Pt and appears lighter.

Figure 7. Specimen mass gain during 1h cycles at 1100°C in dry O_2 and air with 50 and 90vol.% H_2O for (a) coatings on N5 and (b) coatings on 142 and cast Ni-22Al-10Pt-0.4Hf.

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
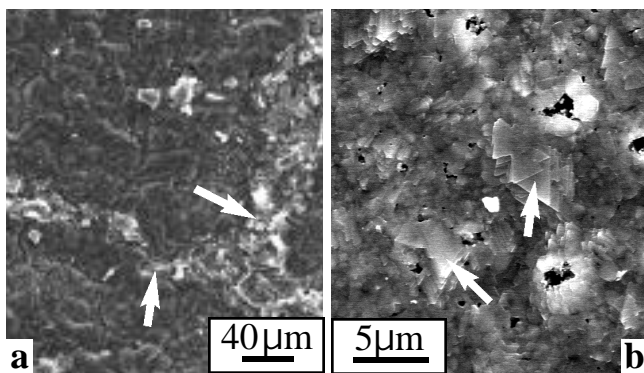

Figure 8. SEM secondary electron plan-view images of the scale formed on 7μm Pt coating on 142 after oxidation at 1100°C for (a) 300, 1-h cycles in air+50%H_2O and (b) 200, 1-h cycles in air+90%H_2O. Arrows in (a) point to spall, in (b) to faceted grains.
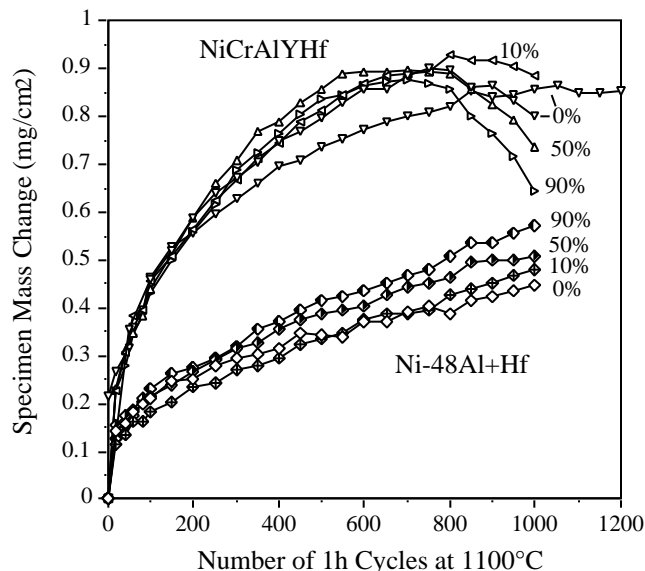

Figure 9. Specimen mass gain for cast Ni-20Cr-10Al+Y,Hf and Ni-48Al-0.05Hf specimens exposed to 1h cycles at 1100°C in dry O_2 or air with various vol.% of H_2O from 10-90%.

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 + ' 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 + ' system.[2,3,5-7] Because of the transient oxide formation and the interdiffusion observed in + ' coatings, the primary interest for this study[23] was on the oxidation behavior of + ' 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 -Al$_2$O$_3$ because of the faster Al diffusion in the substrate and avoid the possible formation of metastable cubic alumina phases such as - Al$_2$O$_3$.[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
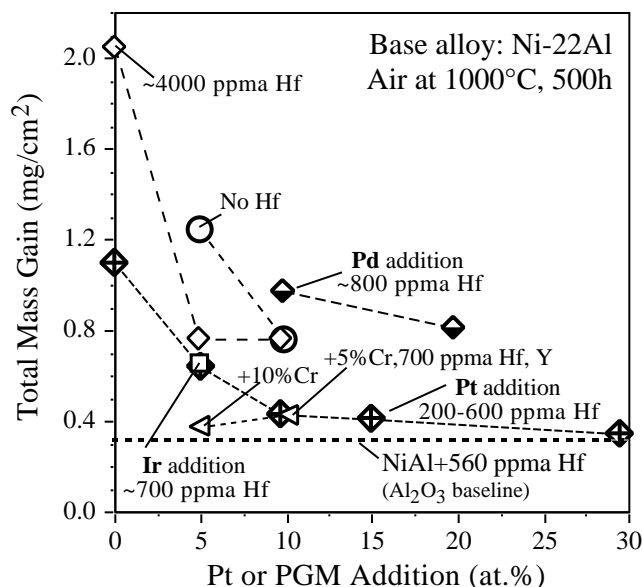
Figure 10. Total mass gain (specimen + spalled oxide) after a 500h isothermal exposure at 1000°C in laboratory air for various precious metal and Hf additions (all in ppm) to alloys with 22at.%Al.

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 θ-Al₂O₃ with its hallmark[31,32] blade-like morphology, Fig. 12b. The metal-oxide interface, Figure 11c, also was irregular because the θ- to α-Al₂O₃ 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 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 Al₂O₃-NiAl₂O₄ interface is thought to be weak because of observations of interfacial voids.[37,38] However, because of the
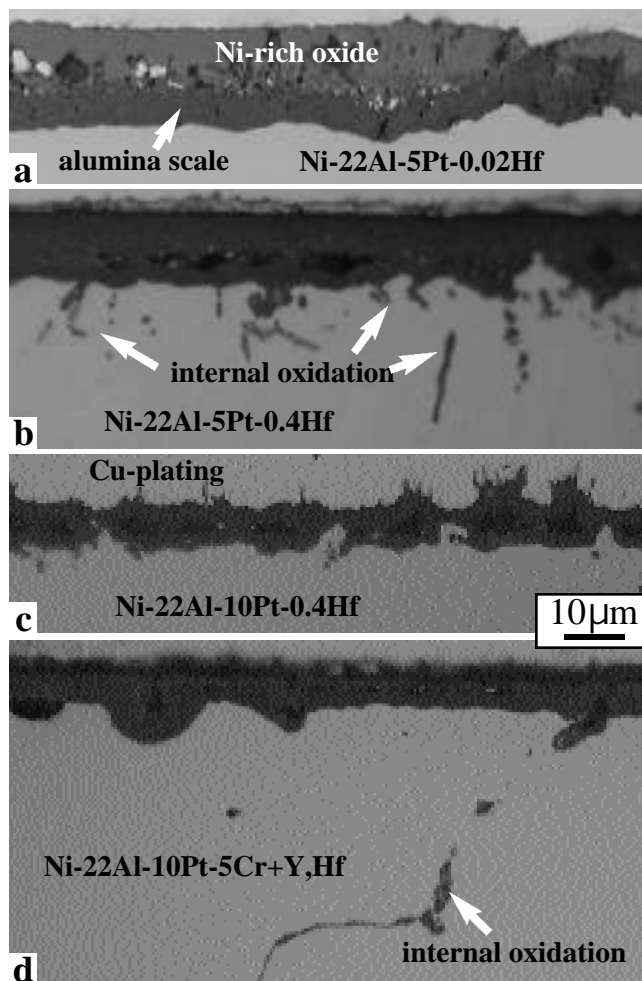

Figure 11. Light microscopy of Cu-plated metallographic sections showing the alumina scale formed after 10, 500h cycles at 1000°C on (a) Ni-22Al-5Pt-0.02Hf, (b) Ni-22Al-5Pt-0.4Pt, (c) Ni-22Al-10Pt-0.4Pt and (d) Ni-22Al-10Pt-5Cr-0.07Y,Hf.
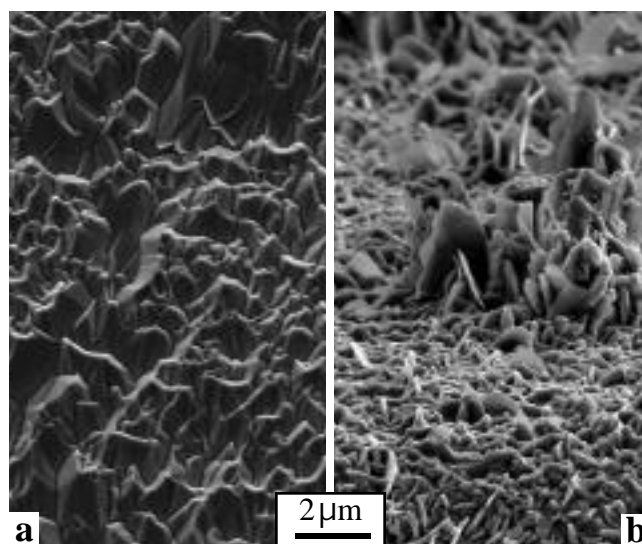

Figure 12. SEM secondary electron images of the scale formed after 10, 500-h cycles at 1000°C in laboratory air on (a) Ni-22Al-5Pt-0.4Hf and (b) Ni-22Al-10Pt-0.4Hf. (b) is tilted.
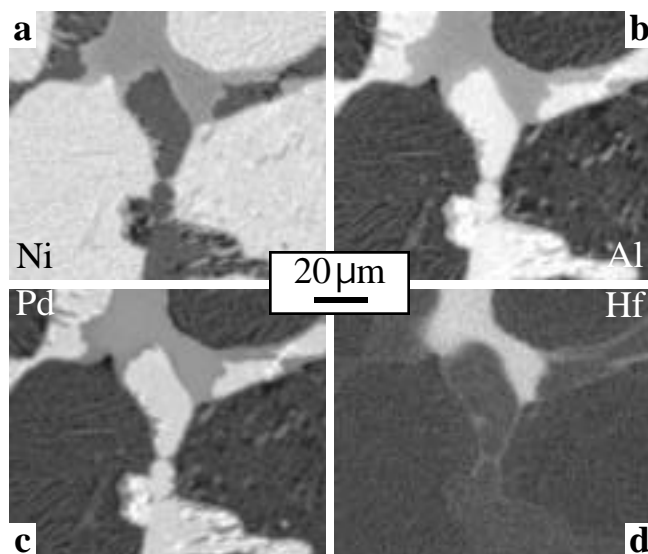
Figure 13. EPMA x-ray maps of the Ni-22Al-20Pd-0.07Hf alloy (a) Ni, (b) Al, (c) Pd and (d) Hf.

Figure 15. Bright field TEM cross-section image of the scale formed on Ni-22Al-30Pt-0.02Hf after 2h at 1200°C. The boundary between the outer spinel layer and the inner alumina layer is marked by a dashed line.

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 α-Al$_2$O$_3$ morphology on β-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 α-Al$_2$O$_3$ phase. Above the α-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 β-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
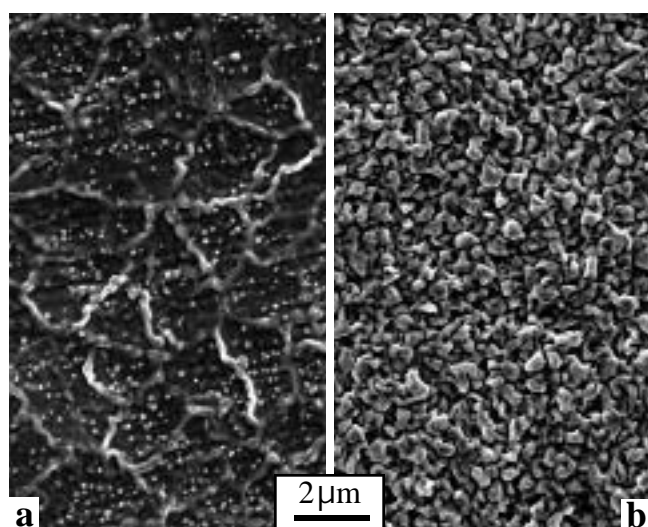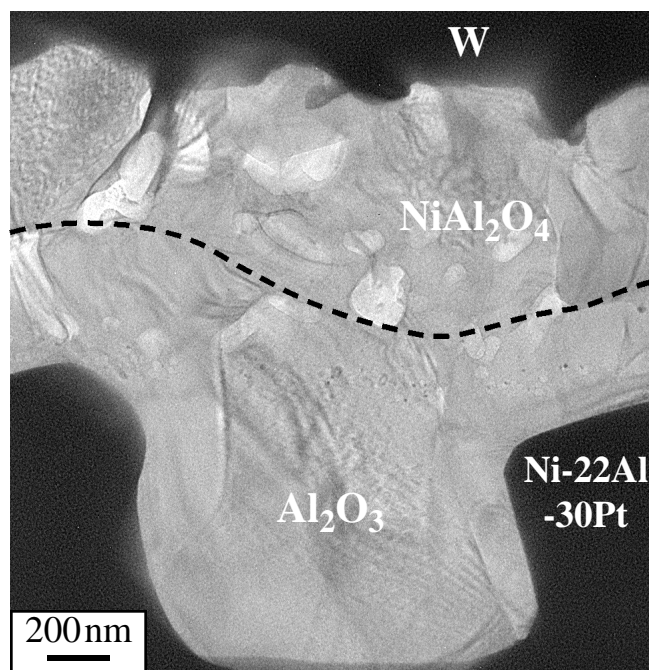

Figure 14. SEM secondary electron plan-view images of the scale formed after 2h at 1200°C in dry O$_2$ on (a) Ni-42Al-0.05Hf and (b) Ni-30Pt-22Al-0.02Hf.
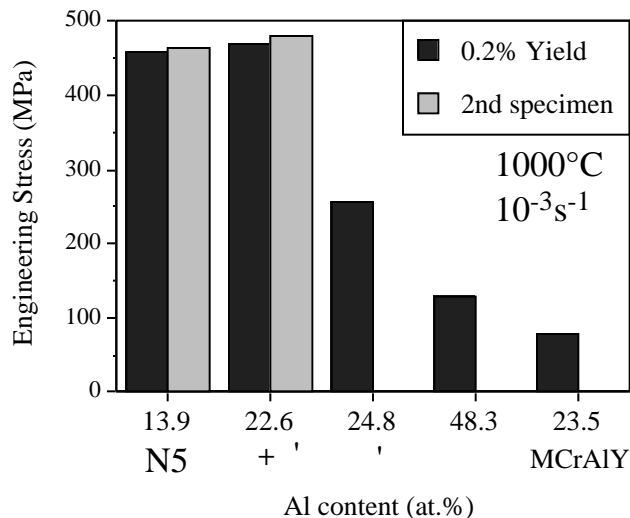
Figure 16. Compression yield stress (0.2%) for various Ni-Al phases with ~500ppma Hf at 1000°C. The Ni-22Al alloy also contained 10%Pt. For comparison, values for alloy N5

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

Figure 17. Mean coefficient of thermal expansion for Ni-22Al-5Pt-0.02Hf (solid line) compared to other alloys and α-Al₂O₃.

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 Ir was beneficial in γ + γ' alloys. Prior work on γ alloys indicated that Ir was more effective in improving scale adhesion than Pt.[42]

In general, the current work suggests that there are some very attractive features for γ + γ' coatings that should be further investigated. The hot corrosion resistance appears 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 I, 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
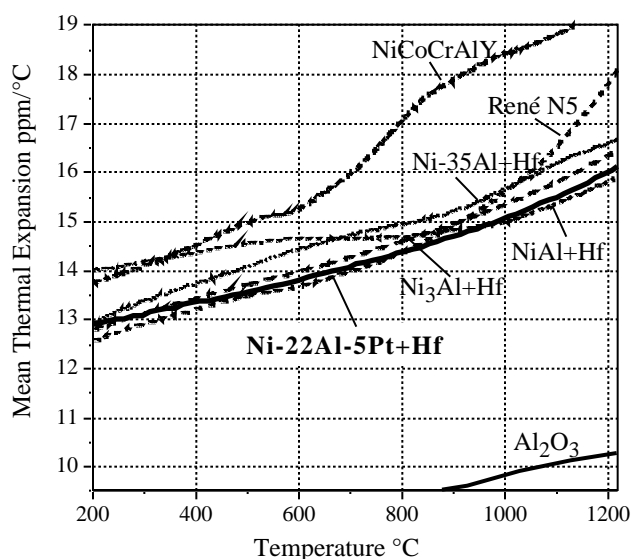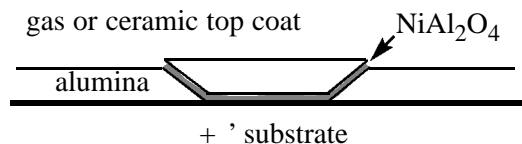
Figure 18. Schematic for scale spallation with a + ' coating or alloy. When the alumina scale spalls, if the substrate initially forms a Ni-rich oxide, the protective oxide layer will be degraded.

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 Ni_3Al 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 + ' 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 + ' coatings for future power generation applications, + ' 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 + ' coatings was much better on N5 substrates in both dry O_2 and with H_2O 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 + ' coating on N5 at 1150°C.

The oxidation performance of model + ' 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 + ' alloy was significantly higher than -NiAl or MCrAlY specimens. The thermal expansion was similar to other Ni-Al compositions.

The current assessment of + ' 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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