

COMPOSITIONALEFFECTS ON ALUMINIDE OXIDATION PERFORMANCE:
OBJECTIVES FOR IMPROVED BOND COATS

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Abstract

In order to achieve long thermal barrier coating lifetimes, underlying metallic bond coats need to form adherent, slow-growing Al_2O_3 layers. A set of guidelines for developing aluminide bond coat compositions is proposed in order to maximize oxidation performance, i.e. forming a slow-growing adherent alumina scale. These criteria are based on results from cast, model alloy compositions and coatings made in a laboratory-scale chemical vapor deposition facility. Aluminide coatings are thought to have more long-range potential because of their lower coefficient of thermal expansion compared to MCrAlYs. The role

of Pt in improving alumina scale adhesion and countering the detrimental role of indigenous sulfur is discussed. However, the improvements associated with Pt are minimal compared to reactive element doping. One strategy which has great promise for improvement is to incorporate Hf into the coating. From an oxidation standpoint, this would preclude the need for Pt in the coating and also reduce the scale growth rate. While excellent oxidation performance was observed for cast Hf-doped NiAl, its benefits can be compromised and even eliminated by co-doping with elements such as Cr, Ti, Ta and Re. Creating a pure Hf-doped NiAl is one promising approach for improving the oxidation performance of bond coats.

Introduction

Formerly, the role of metallic coatings on Ni-base superalloys was simply to limit environmental attack of the underlying substrate. Now, a new paradigm has been established for metallic coatings that have been adapted as bond coats for thermal barrier coating (TBC) systems. It is no longer sufficient that the metallic coating simply minimize the corrosion rate. The metallic coating must form an adherent, slow-growing external Al₂O₃ layer beneath the overlying low thermal conductivity ceramic top coat. The ability of the coating to reform a protective thermally grown oxide or scale in the event of spallation is no longer the key. It is much more important that the scale be developed with a minimum of transient oxides and that it have near-perfect adhesion to limit spallation of the ceramic top coat, thereby achieving a long TBC lifetime.

While oxidation is not the only concern in complex TBC systems, it is, however, a primary factor in developing the next generation of bond coats with longer lifetimes or for engines with higher firing temperatures. Therefore, a set of compositional guidelines for coatings is proposed in order to assist in maximizing oxidation performance. These criteria are based on results from tests in which cast alloy compositions were used to quantify and understand possible improvements as a basis for further investigations using coatings made by chemical vapor deposition (CVD). Experimental work involved furnace cycle testing, isothermal kinetic measurements and in-depth characterization of the alumina scale, including transmission electron microscopy (TEM).

Experimental Procedure

Cast alloys (16mm diameter) were fabricated by vacuum induction melting and solidifying in 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 are listed in atomic percent. After casting, alloys were annealed for 4h at 1300°C in quartz ampules. Oxidation coupons (1-1.5mm thick, typically 15mm diameter) were polished to 0.3µm alumina and cleaned in acetone and methanol prior to oxidation. Aluminide coatings with and without Pt were fabricated by a CVD process on Y-free, René N5 substrates (a General

Electric single crystal superalloy). This low-sulfur coating process is described in detail elsewhere.[1,2]

Isothermal exposures were performed in dry, flowing O₂ and mass gain was measured using a Cahn Instruments model 1000 microbalance. Cyclic testing was performed in two ways.[3] Long-term cycles (100-500h) were conducted in air with specimens in individual pre-annealed alumina crucibles. Crucibles and specimens were cooled to room temperature for >1h before weighing. Short-term (1-10h) cycles were performed in dry, flowing oxygen with specimens attached to alumina rods with Pt-Rh wires. Specimens were cooled for 10min between cycles and the cycle time is the time at temperature. Specimen mass changes were measured using a Mettler model AG245 balance. Hot corrosion testing was performed at 950°C and used 1h thermal cycles. Specimens were coated with 1.0mg/cm² Na₂SO₄ after 1h and 100h. This testing is described in detail elsewhere.[4]

After oxidation, specimens were characterized by field emission gun, scanning electron microscopy (FEG-SEM) equipped with energy dispersive x-ray analysis (EDX). Specimens also were Cu-coated and sectioned for metallography. Scanning transmission electron microscopy (FEG-STEM) equipped with EDX was used to analyze cross-sectional specimens fabricated by focused ion beam milling (FIB).[5] During FIB specimen preparation, a W layer is deposited to protect the gas interface of the scale. Thermal expansion measurements were performed on specimens (3mm diameter, 1cm or 2.5cm long) of several alloys up to 1200°C on a Theta Industries dual push rod differential dilatometer.

Results

These results focus on nickel aluminide compositions. While MCrAlY-based coatings represent an important class of coatings for current applications, results from this lab suggest that scale adhesion on MCrAlYs is inherently inferior to that on aluminides at 1100°-1200°C[6,7] and therefore this coating approach does not represent the most fruitful option for developing high temperature bond coats. Figure 1 compares the temperature dependence of the coefficient of thermal expansion (CTE) of René N5 (Table I) and castings of generic bond coat compositions: NiAl+Hf and NiCoCrAlY. While the CTEs for René N5 and NiAl+Hf are reasonably similar, that for NiCoCrAlY was found to be significantly greater at temperatures above 600°C. These results

	Ni	Al	Hf	Pt	Cr	C	S(ppma)	Other
Ni-40Al	59.68	40.27	<0.01	--	<0.01	0.04	<4	
Ni-42.5Al	57.34	42.61	<0.01	--	<0.01	0.04	<4	
Ni-50Al	49.91	50.05	<0.01	--	<0.01	0.04	<4	
Ni-51Al	48.67	51.22	<0.01	--	<0.01	0.04	4	0.01Fe, 0.06Si
Ni-40Al+Hf	59.79	40.11	0.05	<0.01	<0.01	0.04	<4	
Ni-42.5Al+Hf	58.00	41.90	0.05	<0.01	<0.01	0.04	<4	
Ni-50Al+Hf	49.83	50.07	0.05	--	0.01	0.04	<4	
NiAl-2Pt	47.36	50.21	0.005	2.35	<0.01	0.04	4	0.01Fe, 0.01Cu
NiAl-5Pt	45.10	49.60	<0.01	5.20	0.05	0.04	9	
NiAl-2Pt+Hf	47.78	49.71	0.05	2.35	0.03	0.04	4	0.01Cu
NiAl-2Cr+Hf	48.28	49.63	0.05	<0.01	2.00	0.04	4	
NiAl-5Cr+Hf	47.76	47.20	0.05	<0.01	4.95	0.04	8	
NiAl-10Cr+Hf	45.13	45.07	0.05	<0.01	9.70	0.04	5	0.01Fe
NiAl-1Re+Hf	48.37	50.53	0.04	--	<0.01	0.04	1	1.00Re, 0.02Si
NiAl-1Ta+Hf	48.67	50.15	0.05	--	<0.01	0.04	4	0.92Ta, 0.14Fe, 0.01Co
NiAl-1Ti+Hf	48.58	50.33	0.05	--	<0.01	0.04	1	1.00Ti, 0.01Fe
René N5	64.85	13.88	0.05	--	7.79	0.25	7	2.1Ta, 7.3Co, 1.6W, 1.0Re, 0.1Y
NiCoCrAlY	40.38	23.49	<0.01	--	17.43	0.04	8	18.48Co, 0.15Y, 0.01Ti

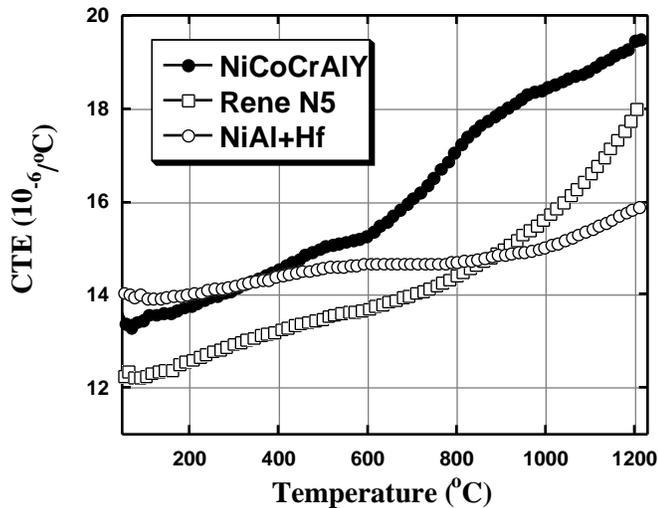


Figure 1. Coefficient of thermal expansion data for 3 alloys from 25°-1200°C. The aluminide specimen had the lowest expansion from 900°-1200°C.

are similar to earlier work.[8] Since the thermal stress in the alumina scale is related to the CTE difference, the additional thermal expansion compared to that for alumina ($9 \times 10^{-6} \text{°C}^{-1}$) represents a significant increase in thermal stress. Such a problem cannot be solved by reactive element (RE) doping or impurity control (e.g. S) and thus is an inherent limitation of the MCrAlY class of materials. Therefore, this work attempts have been made to understand and optimize the oxidation performance of aluminide coatings.

Current Compositions: The Pt Effect

Current aluminide bond coats often contain Pt, which is now commonly added in conjunction with a low activity CVD aluminization process which results in a single phase $-(\text{Ni,Pt})\text{Al}$ coating.[9] The role of Pt in oxidation has not been fully explained but it is clear from recent results on both cast aluminides[10] and CVD aluminide coatings[2] that Pt improves alumina scale adhesion. This beneficial effect is shown at 1100°C for cast aluminides, Figure 2. With the addition of 2 or 5 at% Pt (10 or 20wt%), very little scale spallation was observed after 1000 cycles. Under the same conditions, undoped NiAl showed significant scale spallation. When Pt was added to CVD aluminide coatings, Pt mitigated the detrimental role of sulfur, present in the superalloy (Y-free René N5) substrate, on scale adhesion, Figure 3. Previous work on CVD NiAl coatings (without Pt) had shown that substrate sulfur content had a significant effect on alumina scale adhesion.[1] This result suggests that Pt somehow counters the detrimental role of S. One suggested mechanism for the effect of S on scale adhesion is that it increases the growth of interfacial voids.[11,12] The addition of Pt to CVDNiAl appeared to have reduced or eliminated this type of void growth, thereby improving contact between the metal and scale.[13]

The comparison of simple and Pt-modified CVD aluminide coatings on René N5 also demonstrated that Pt did not (1) reduce the alumina scale growth rate, (2) alter the diffusion of heavy elements into the coating during deposition or oxidation, or (3) alter the coating Al content before or after oxidation.[2,13].

Another area where the addition of Pt did not appear to play a strong role was hot corrosion resistance.[14] Figure 4 shows

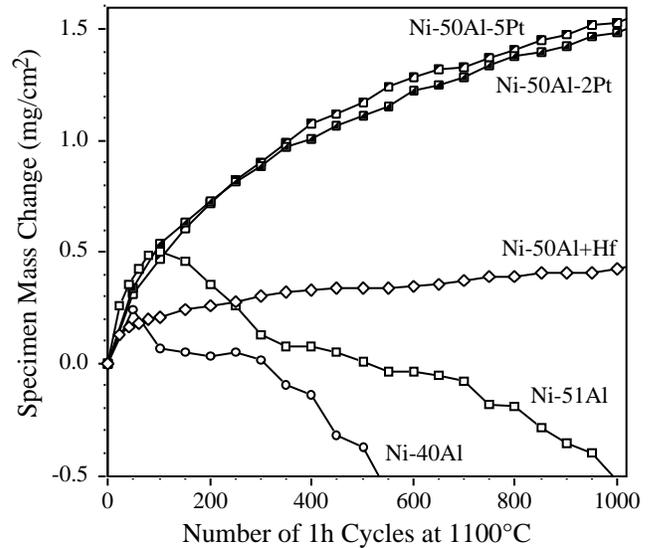


Figure 2. Specimen mass changes for various Ni-Al alloys during 1h cycles at 1100°C in O_2 . The addition of Pt significantly improved scale adhesion compared to simple aluminides without Hf. The addition of Hf improved scale adhesion and reduced the scale growth rate.

results from testing at 950°C with a $1.0 \text{mg/cm}^2 \text{Na}_2\text{SO}_4$ coating applied after 1h and 100h. Additions of Pt did not alter the behavior compared to NiAl+Hf. Only the addition of Cr improved performance. While Pt-modified aluminide coatings may be superior to simple aluminide coatings in hot corrosion due to a second order effect of improved alumina scale adhesion, there is no chemical effect of Pt in improving hot corrosion resistance. The Cr content of the coating is the critical component.

To provide additional information on the role of Pt on scale adhesion, TEM cross-sections were prepared of the scale formed on NiAl-5Pt after 2h at 1200°C in O_2 . These conditions were selected to develop a $1\text{-}2 \mu\text{m}$ thick oxide layer which is fully phase and to allow comparison with previous work. In general the scale was $1\text{-}1.5 \mu\text{m}$ thick and no transient Ni-rich oxide was observed. As surmised from the good scale adhesion, there were no interfacial voids observed in the thin area, Figure 5. The scale

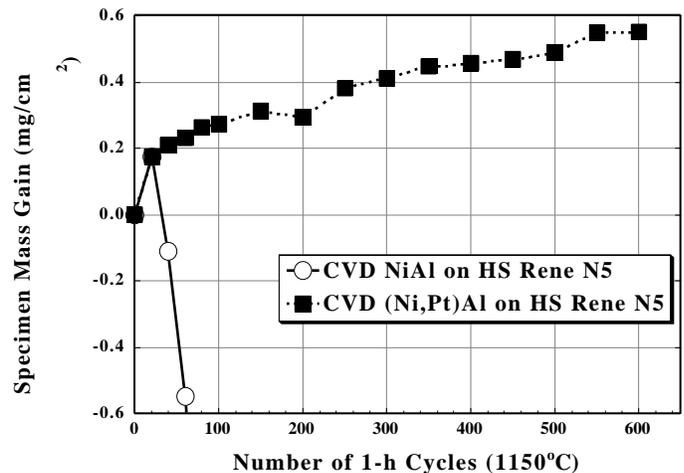


Figure 3. Specimen mass changes during 1h cycles at 1150°C for CVD aluminide coatings with and without Pt on a Y-free René N5 substrate that was not de-sulfurized (4 ppm S).

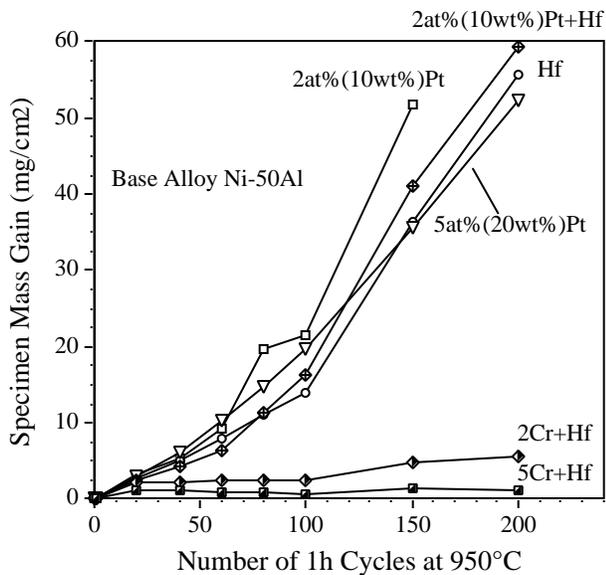


Figure 4. Hot corrosion specimen mass gains at 950°C for cast NiAl alloys with various modifications. All specimens were coated with 1.0mg/cm² Na₂SO₄ after 1h and 100h. Chromium had a beneficial effect but Pt and Hf showed no benefit.

was generally two grains thick with the outer grains containing more voids than the inner, more columnar grains.

The most interesting feature of the scale was the roughness of the metal-scale interface, particularly the metal protrusions extending into the oxide. Protrusions have been observed previously for both cast Pt-Al alloys [15] and for CVD Pt aluminide coatings.[2] Each protrusion was centered on a single alumina grain and extended into it. This is seen clearly in a STEM annular dark field image, Figure 6. As transport occurs primarily along alumina grain boundaries at this temperature, one explanation for the formation of these protrusions is that new oxide is forming rapidly at the

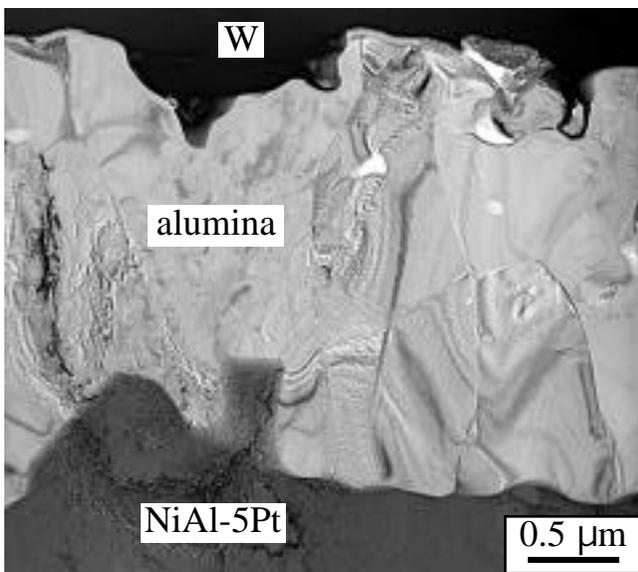


Figure 5. TEM bright field image of the alumina scale formed on NiAl-5Pt after 2h at 1200°C. In general, the scale is two grains thick and neither the gas interface or metal interface of the scale is smooth. The W coating is part of the FIB specimen preparation.

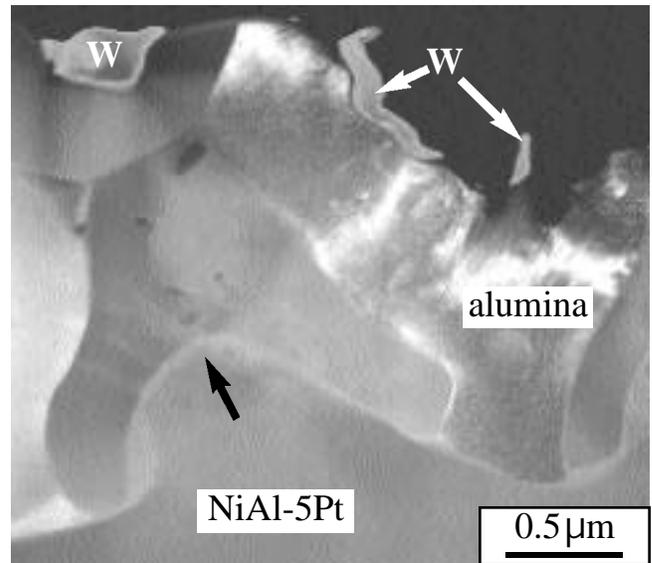


Figure 6. STEM annular dark field image of the alumina scale formed on NiAl-5Pt after 2h at 1200°C. Above the metal protrusion (arrow) is a single alumina grain. Small remnants of the FIB-process W coating remain at the gas interface of the scale.

junction of oxide grain boundaries and the metal. If lateral oxygen diffusion does not keep up with this process, the interface will not remain flat. Inward growing ridges have been observed on undoped NiAl [16] and when the oxide loses contact with the metal due to interfacial void formation.[12] The ridges have been proposed to grow by a similar mechanism where lateral diffusion cannot keep up with the inward grain boundary diffusion of oxygen.[12] In this case where no voids form, the ridges appear to grow into the substrate leaving metal protruding into the center of the oxide grain. While the structure looks like the metal grew into the oxide, it may actually be metal remaining from a non-uniform oxidation front. The gas interface of the scale also was rough. This

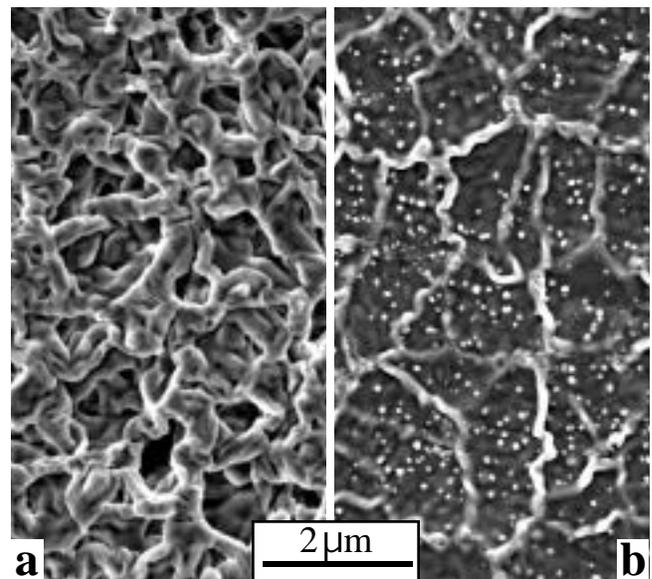


Figure 7. FEG-SEM plan-view images of the alumina scale formed after 2h at 1200°C on (a) NiAl-5Pt and (b) NiAl-2Pt+Hf. The “intrinsic” ridges in (a) are much wider and form due to outward Al transport. The “extrinsic” ridges in (b) remain from the β phase transformation.

is typical of undoped alumina scales (those formed on substrates without a RE dopant) which form a network of closely spaced “intrinsic” ridges (Figure 7a) at this temperature due to the outward diffusion of Al.[17,18] Thus, the adherent alumina scales on (Ni,Pt)Al are attributed to the elimination of voids at the metal-scale interface and the metal protrusions into the scale acting as a mechanical interlock.

Ideal Alumina-Formation: The Hf Effect

While Pt is beneficial to alumina-scale adhesion, its overall influence on oxidation behavior is minimal compared to that of an optimized RE addition, particularly 0.05% Hf.[10] (Yttrium is not considered a viable alternative to Hf for aluminides because it readily forms NiY_x precipitates, which internally oxidize and disrupt scale formation.[19]) Hafnium not only improves alumina scale adhesion but also has been shown to reduce the scale growth rate by an order of magnitude compared to undoped -NiAl [10,20]. This effect is evident in Figures 2 and 8 when comparing the cyclic oxidation behavior of Pt-doped NiAl to Hf-doped NiAl. Both alloys form adherent alumina scales at 1100°C but, because the scale on NiAl+Hf grows more slowly, it has a significant long-term advantage. There is some critical scale thickness where the thermal cooling strains will exceed the interfacial strength and scale spallation cannot be avoided. Empirical models have suggested critical scale thicknesses in the 10-15 μm range (corresponding to 2-3 mg/cm^2), e.g. Ref.21. After 1000h at 1100°C, this level has not been reached. However, at 1150°C, this limit is attained for Pt-doped NiAl and spallation was observed to occur after less than 1000, 1h cycles, Figure 8. With the slower growing scale on Hf-doped NiAl, the critical scale thickness will not be reached for thousands of hours. No additional benefit was observed from combining Pt- and Hf-doping, Figure 8.

The scale microstructure formed on Hf-doped NiAl was investigated by TEM. On this substrate, the scale was thinner and had fewer internal voids than that formed on NiAl-5Pt (compare Figures 5 and 9). The addition of Hf is believed to act like Zr and inhibit the outward Al boundary transport,[17] resulting in growth

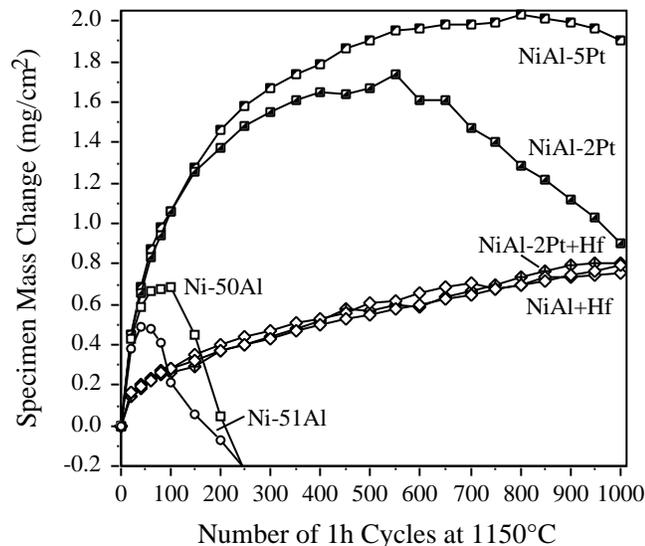


Figure 8. Specimen mass changes for various Ni-Al alloys during 1h cycles at 1150°C in O_2 . The addition of Pt significantly improved scale adhesion compared to simple aluminides without Hf. The addition of Hf improved scale adhesion and reduced the scale growth rate.

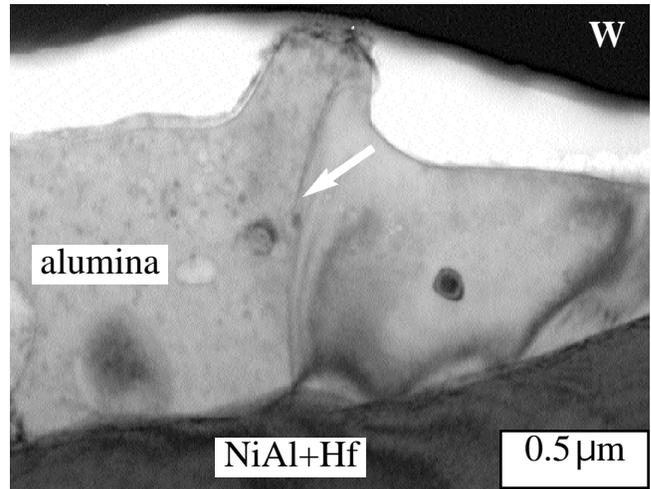


Figure 9. TEM bright field image of the alumina scale formed on NiAl+Hf after 2h at 1200°C. Grain boundaries (arrow) are associated with the ridges at the gas interface and the scale is only one grain thick. The W coating was part of the FIB preparation.

primarily by inward grain boundary diffusion of oxygen. This eliminates the intrinsic ridges and leaves only the “extrinsic” ridges[18,22] from the α phase transformation, Figure 7b. At each of the extrinsic ridges, a grain boundary was observed as predicted.[22] Using STEM/EDX, Hf ions were detected as segregants to the scale grain boundaries and the metal-scale interface. Similar behavior has been observed for all RE additions.[7,10,17,23-30] The segregation of Hf ions is the most likely explanation for the low scale growth rate; however, its benefit over other dopants (e.g. Y and Zr), which also segregate at similar levels, has not been explained.

Thus, a promising approach to improved coating performance would be to incorporate Hf at the appropriate level in an aluminide coating, thereby achieving a significant improvement in alumina scale adhesion and making the addition of Pt unnecessary, at least from the viewpoint of oxidation behavior.

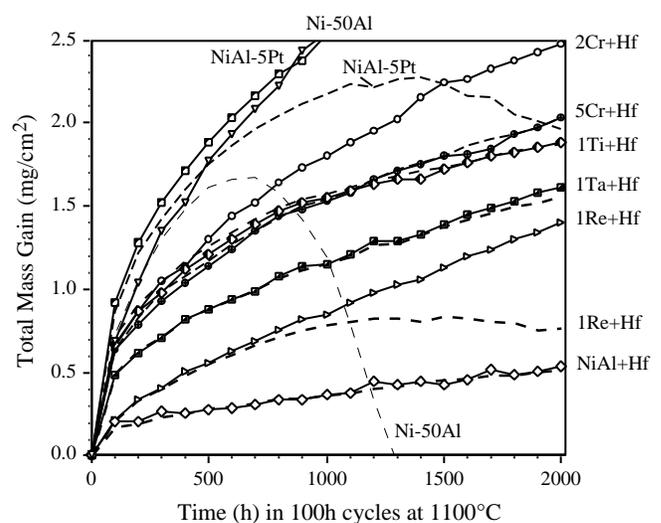


Figure 10. Total mass gain (specimen + spall) for various alloys during 100h cycles in alumina crucibles at 1100°C. Dashed lines show specimen mass changes. Higher total mass gains indicate higher scale growth rates or more scale spallation.

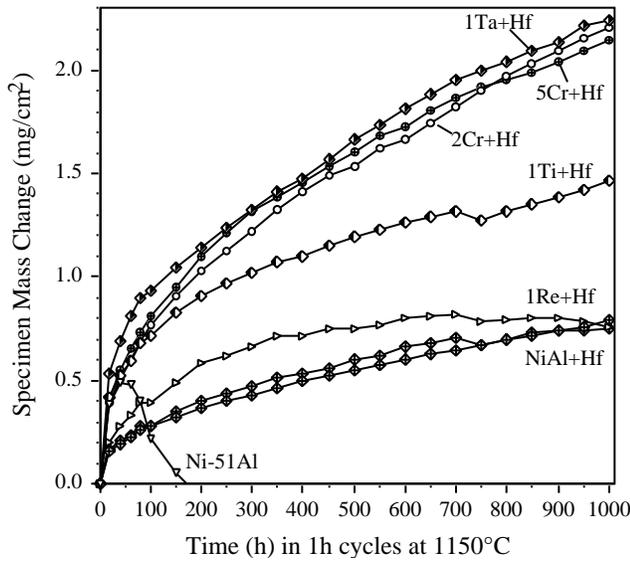


Figure 11. Specimen mass changes for various Ni-Al alloys during 1h cycles at 1150°C in O₂. The addition of Hf improved scale adhesion and reduced the scale growth rate. When secondary dopants were added, the scale growth rate increased.

Real World Coatings: Co-Doping Effects

The major problem with the Hf-doping approach is that current aluminide coatings contain numerous other elements besides Ni and Al due to interdiffusion with the superalloy substrate.[1] The benefits of Hf can be compromised if additional elements are also incorporated into the coating. Strong detrimental effects were found from the addition of 1%Re and 2-5%Cr to Hf-doped NiAl, Figures 10-12. Lesser negative effects were observed for additions of 1%Ti or Ta. The data shown in Figure 10 for 1100°C are from 100h thermal cycles which were used to simulate the longer duty cycles used for land-based gas turbines for power generation. The total mass gain reflects the metal wastage by summing the

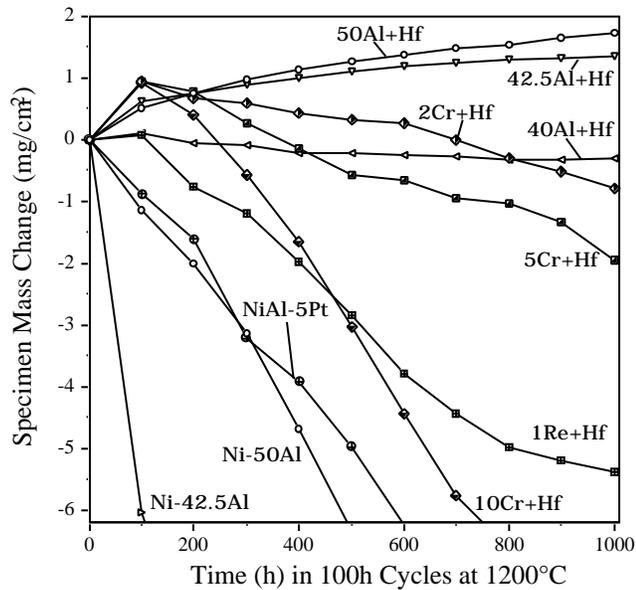


Figure 12. Specimen mass changes during 100h cycles at 1200°C in air. While Hf improves Ni-Al scale adhesion, additions of Re and Cr degrade it.

specimen mass gain and spalled scale inside the alumina test crucible. The difference between the total (solid line) and specimen (dashed line) mass gains reflects the amount of scale spallation. The lowest total mass gain was for NiAl+Hf. Higher mass gains were measured for NiAl-1Re+Hf due to some scale spallation and for NiAl with other co-dopants because of an accelerated scale growth rate (and little scale spallation). A similar observation is made for 1h cycles at 1150°C, Figure 11. Very little scale spallation was observed for Cr- or Ta-doped NiAl+Hf but the scale growth rate was 3-4X that for NiAl+Hf. At 1200°C, the additions of Cr and Re were found to cause significant scale spallation during 100h cycles, Figure 12. Thus, the improvements associated with Hf-doping can be compromised to various degrees by other dopants.

After 1000, 1h cycles at 1150°C, various co-doped NiAl specimens were sectioned, Figure 13. As expected from the mass change data, the scale on NiAl+Hf was thinnest. The addition of Ta, Ti and Cr resulted in a thicker but adherent scale with an indication of

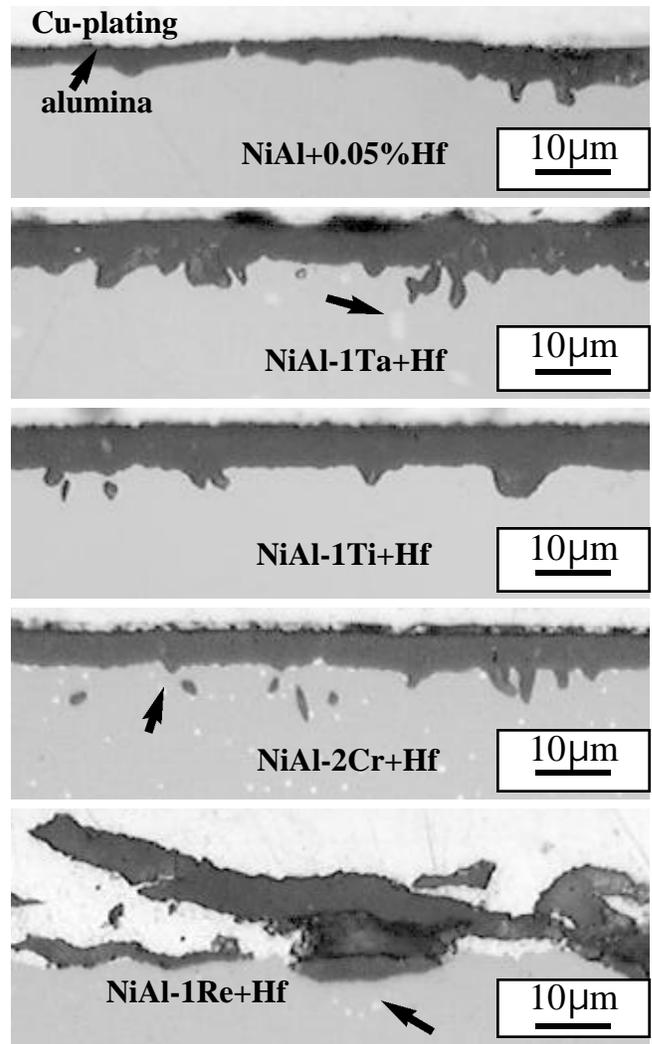


Figure 13. Copper-plated metallographic cross-sections of surface scale after 1000, 1h cycles at 1150°C on (a) NiAl+Hf; (b) NiAl-1Ta+Hf, (c) NiAl-1Ti+Hf (d) NiAl-2Cr+Hf and (e) NiAl-1Re+Hf. The scale on Hf-doped NiAl was thinner as expected from the mass change data. Precipitates (arrows) are noted with the addition of Ta, Re or Cr.

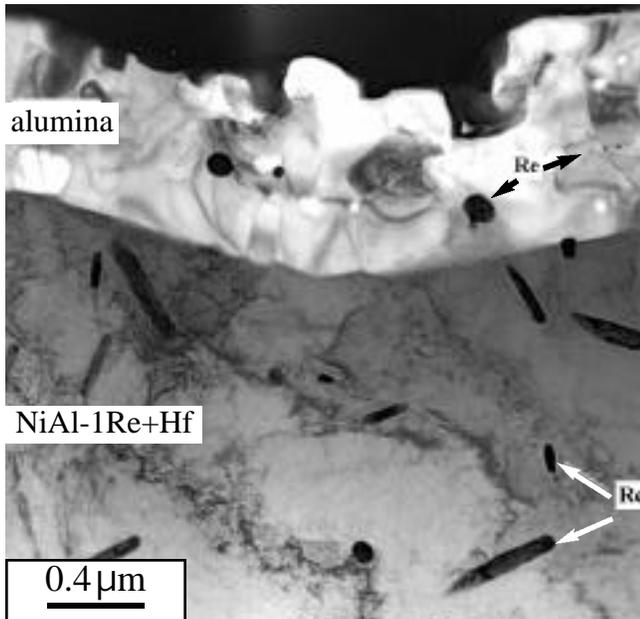


Figure 14. TEM bright field image of the alumina scale formed on Ni-50at%Al-1Re-0.05Hf after 2h at 1200°C in O₂. Re-rich precipitates are observed in the metal and in the oxide.

more oxide penetrations into the substrate in each case, Figures 13b-d. Some penetrations contain additional Ta- or Ti-rich oxide particles. The scale on NiAl-1Re+Hf showed significant scale spallation which also was evident in the mass change data, Figure 11. Additions of Ta, Re and Cr all resulted in precipitate formation in the substrate (arrows in Figures 13b, d & e).

The same alloys were sectioned for TEM analysis after oxidation for 2h at 1200°C. Compared to the scale on NiAl+Hf, Figure 9, the Ti and Ta additions showed little effect on the scale microstructure under these conditions. Using STEM/EDX, both Ta and Ti ions were found as boundary segregants along with Hf. The Cr- and Re-doped specimens were of more interest as these elements promoted scale spallation at 1200°C, Figure 12. Both elements formed precipitates in the γ -matrix which appeared to disrupt scale adhesion. For NiAl-1Re+Hf, γ -Re particles were observed

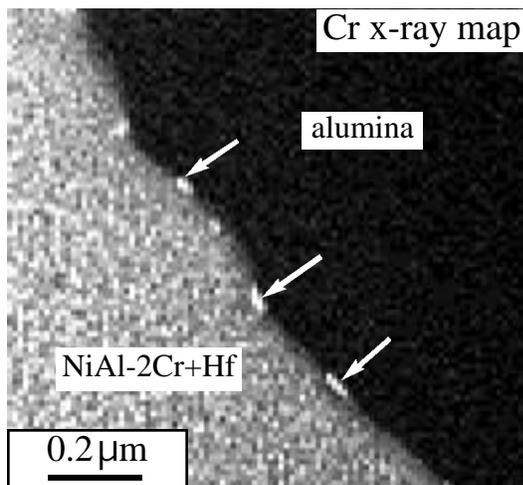


Figure 15. High resolution STEM Cr x-ray map of the scale formed on Ni-49Al-2Cr-0.05Hf after 2h at 1200°C in O₂. Arrows mark γ -Cr precipitates at the metal-oxide interface.

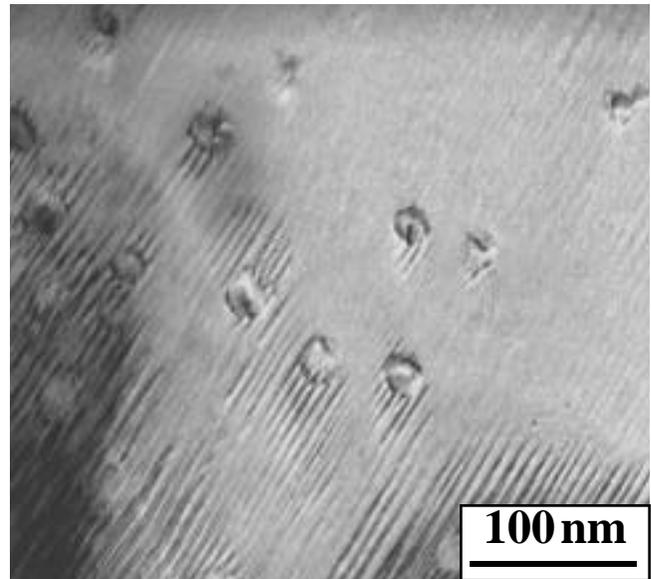


Figure 16. TEM bright field image of a CVD simple aluminide coating on a René N5 substrate after 100h at 1150°C. Cr-rich precipitates are observed throughout the coating.

in the metal and in the oxide, Figure 14, suggesting a low solubility of Re in the γ phase. After a 100h exposure at 1200°C, interfacial voids were observed by SEM but, after only 2h, there was no indication of interfacial void formation in the TEM section. In general, the scale microstructure was very different with coarse ridges and two grains in thickness, much like that on Pt-doped NiAl, Figure 5. The scale formed on NiAl-2Cr+Hf had a very similar microstructure to that formed on NiAl+Hf and Hf ions were detected as oxide grain boundary and metal-oxide interface segregants. The only difference noted was the presence of small (30-50nm) γ -Cr particles at the metal-scale interface. These particles are shown in the STEM-EDX Cr x-ray map in Figure 15. Based on metallographic observations of other Cr-doped alloys, these particles appear to increase in size with exposure time and temperature, e.g. Figure 13e. These precipitates are not observed in as-cast NiAl-2Cr+Hf. Their nucleation may be a result of Cr becoming enriched in the near-surface region as it is rejected from the oxidation front. Since the CTE of γ -Cr is much lower than γ , [31] the precipitates may cause an additional strain during cooling. Similar Cr-rich precipitates were also observed in both simple and Pt-modified aluminide coatings, after 100h at 1150°C, Figure 16. Thus a similar mechanism is likely operating in CVD aluminide coatings with these precipitates having a negative effect on scale adhesion.

An additional issue in the development of CVD aluminides is that typically the coatings do not contain 50at%Al (31.5wt%) as did these cast aluminides. A coating will also lose Al during high temperature exposure by diffusion into the substrate. After only 100h at 1150°C, γ formation was noted by TEM at CVD Pt-modified aluminide grain boundaries, indicating significant Al loss.[13] Ni₃Al has significantly worse scale adhesion than NiAl, even when RE-doped.[19,32] This also has been attributed to its higher CTE than NiAl.[22] In order to explore the effect of Al content within the γ phase field, Hf-doped Ni-Al alloys were cast with Al contents down to 40at%Al, Table I. Doping with Hf significantly improved the performance of undoped, low Al content (40-42.5at%) NiAl, Figure 12. However, the mass loss observed for Ni-40Al+Hf suggests that it may be more prone to spallation than higher Al content NiAl. This aspect is still being

explored with microstructural characterization and lower (35%) Al content alloys. Because castings, unlike coatings, do not lose Al by back diffusion, results from castings may not be entirely representative of coating behavior.

Discussion

These results have been compiled in order to suggest some composition guidelines that may lead to bond coats with improved performance. The guidelines relate to oxidation performance and may be altered by mechanical property or other considerations involved in maximizing TBC performance. They are intended as a starting point for an overall discussion of TBC system design and performance.

From an oxidation standpoint, an aluminide coating appears to have greater potential than MCrAlYs for use as a bond coat. Though not well recognized, the alumina scale adhesion on NiCrAlY-type alloys is decidedly inferior to that formed on RE-doped NiAl or FeCrAlY.[6,7] Cast NiCrAlY spalls readily at 1100°C while RE-doped NiAl only spalls after >1000 h cycles at 1200°C. While Pt does improve scale adhesion in aluminides, its potential is limited compared to Hf additions. (One attractive feature of Pt is that it is easily incorporated into a CVD aluminide coating, unlike Hf.) Many of the beneficial effects often attributed to Pt, such as reducing heavy element diffusion into the coating or increasing the Al content of the coating, have not been confirmed experimentally.[2,13] One issue that requires further study is the interaction between Pt and S. Understanding this mechanism may provide useful insight into the role of S in high temperature oxidation.[33,34]

The incorporation of Hf into aluminide coatings offers significant improvements in performance and could preclude the use of Pt. The 0.05Hf level used in this study is sufficient to be uniformly included in the alloy while avoiding excessive internal oxidation associated with higher Hf contents. The best performance would likely be achieved with a coating that only contained Ni, Al and Hf. Incorporation of additional elements would inhibit the potential of Hf to improve scale adhesion and, more importantly, to reduce the scale growth rate. The ultimate benefit of proper Hf-doping is the order of magnitude drop in the scale growth rate. The reduction in rate allows longer time at temperature or higher temperature operation before a critical scale thickness is formed where spallation occurs.

The weak point of a pure NiAl+Hf coating would be hot corrosion. Chromium was the only element which appeared to improve the hot corrosion resistance of NiAl (Figure 4). However, Cr increased scale spallation and the isothermal scale growth rate compared to NiAl+Hf, Figures 10-12. These effects are in good agreement with previously reported work.[35-37] Based on the available data for cast aluminides, it appears that hot corrosion resistance and exceptional scale spallation resistance are mutually incompatible goals for coating performance.

A pure NiAl+Hf coating will be difficult to produce by traditional CVD coating processes. Since elements detrimental to scale growth and adhesion, such as Cr and Re, incorporate into both inward and outward growing aluminide coatings, the coating essentially must be formed by depositing Ni as well as Al, with a uniform, low level of Hf in the coating. This strategy would allow the formation of an initial scale doped solely by Hf and would require diffusion of substrate elements (e.g. Ta, Cr, Re) to the gas side of the coating before they could negatively impact oxidation performance. Of course, a stable diffusion barrier between the

substrate and coating would further improve this strategy by reducing outward and inward diffusion, but the development of such a barrier appears unlikely.

Attempting to incorporate Hf by surface modifications of the coating is not an appropriate strategy. Ion implantation[38] and RE surface oxide coatings[39] have been shown to be ineffective alternatives to a uniform RE distribution in the substrate.[40] A model for the role of RE dopants on alumina scales suggests that a uniform, constant flux of RE ions diffusing from the substrate into the oxide scale is necessary to maintain the RE benefit.[25]

A final point is that there appears to be no inherent problem with a thick (125 μ m, 5 mil) ceramic coating adhering to a metallic substrate. A 125 μ m-thick, physical vapor deposited, Y₂O₃-stabilized ZrO₂ coating on Zr-doped -NiAl[41,42] had a 20% coating spallation lifetime of 3600, 1h cycles at 1150°C and has not reached 20% spallation after 800, 2h cycles at 1200°C. These observations indicate that an extended coating lifetime should result from the formation of an adherent alumina layer. Current bond coats simply do not form alumina scales with sufficient adherence. The next generation of bond coats will require more careful compositional control in order to achieve significant improvements in performance.

Summary

Based on experimental results from cast aluminides and laboratory-scale CVD aluminide coatings, it appears that single-phase aluminides have a greater potential for the development of improved bond coats than do MCrAlY-based compositions. A series of guidelines is proposed for aluminide coating compositions:

- (1) The main features desired in a bond coat to maximize oxidation performance are:
 - rapid formation of an -Al₂O₃ scale with no transient oxides
 - excellent scale adhesion
 - low rate of scale growth
 - minimal transport of additional elements into the oxide scale
- (2) Pt incorporation provides improved scale adhesion and increases time to first spallation apparently by countering the detrimental role of indigenous sulfur.
- (3) Reactive element (Hf) doping of aluminides results in a reduced rate of scale growth
- (4) No synergistic benefits are anticipated from co-doping Pt and Hf.
- (5) Transport of elements such as Cr, Re, Ti and Ta to the oxide scale can lead to an increase in oxidation rate and a decrease in resistance to scale spallation.
- (6) Within the -phase, Al contents of 50at% Al show better scale adhesion than lower (40at%) Al contents.

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