THE DEVELOPMENT AND PERFORMANCE OF NOVEL Pt+Hf-MODIFIED γ' -Ni₃Al+ γ -Ni BOND COATINGS FOR ADVANCED THERMAL BARRIER COATINGS SYSTEMS

N. Mu^{1,2}, T. Izumi^{1,3}, L. Zhang^{1,4}, and B. Gleeson^{1,2}

¹Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA

²Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15261, USA

³Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

⁴GE Aviation, McAllen, TX 78503, USA

Keywords: γ' -Ni₃Al, Platinum, Ni-based Superalloy, Reactive Element

Abstract

This paper reports results from a larger study that has focused on the development of novel Pt+Hf-modified γ -Ni+ γ' -Ni₃Al-based compositions for high temperature bond coatings with improved reliability and durability. The effects of Pt, Hf and Cr contents on resistance to both isothermal and cyclic oxidations at 1150°C in air were analyzed. It was found that Pt contents of up to 20at.% significantly enhanced the selective oxidation of aluminum so as to suppress the formation of less-protective NiO and NiAl₂O₄. The Pt also served to decrease the reactivity of Hf in the γ' phase, to the extent that unwanted HfO₂ formation could be suppressed. Balanced Pt+Hf-modified γ + γ' compositions exhibited remarkably slow oxidation kinetics. Moreover, γ + γ' coatings were shown to offer clear potential advantages over β -NiAl-based coatings, with the former exhibiting excellent surface stability (*i.e.*, no rumpling) and compatibility with the superalloy substrate (*i.e.*, no SRZ formation).

Introduction

The development of most advanced superalloys has been largely driven by the goal of achieving improved mechanical properties. The engineering solution for imparting oxidation resistance to these alloys has been to apply a protective coating. In the case of state-of-the-art thermal barrier coating (TBCs) systems, it is essential for the inner metallic bond coat to be stable and highly resistant to high-temperature oxidation in order to achieve extended service life [1,2,3]. Accordingly, the requisite thermally grown oxide (TGO) scale on the metallic coating is generally regarded to be α -Al₂O₃.

Considerable past research has focused on the deposition and oxidation behavior of metallic coatings based on the ordered intermetallic compound β -NiAl [4]. Such coatings are excellent Al₂O₃-scale formers and are used extensively in advanced TBC systems for aero-engine applications. There are, however, limitations associated with β coatings when subjected to extended thermal exposures. Two key limitations are surface instabilities (*e.g.*, rumpling) and interdiffusion with the Ni-base superalloy substrate. The former can cause the spallation of the ceramic top coat of the TBC system, while the latter can lead to the formation of unwanted topologically close-packed (TCP) phases and a secondary reaction zone (SRZ) [5,6,7]. Third-generation superalloys and higher have been shown to be particularly prone to extensive TCP and SRZ formations when coated with a β -based composition [3].

The limitations of β -based coatings impose the need for alternative bond coat compositions that could form a protective Al₂O₃ scale and potentially also greatly improve TBC reliability and durability. Gleeson *et al.* [8] recently investigated the Ni-Al-Pt ternary system and found that certain Pt-modified γ' -Ni₃Al+ γ -Ni compositions exhibit oxidation resistance comparable to that of Pt-modified β -NiAl. Moreover, the further addition of hafnium to the Pt-modified γ + γ' alloys was found to decrease the rate of protective Al₂O₃-scale growth by around an order of magnitude. The ability of forming an adherent and slow-growing Al₂O₃ scale and to have phase compatibility with most Ni-based superalloys present major potential advantages of Pt+Hf-modified γ + γ' coating compositions.

Previous research conducted by our group [8,9,10,11] has focused on understanding the chemical effects of Pt and Hf on the interdiffusion and oxidation behavior of γ + γ' bulk alloys. Complementing these bulk-alloy studies has been the development of a process to deposit Pt+Hf-modified γ + γ' -based coatings on Ni-based superalloys. The aims of the current study were to: 1) examine in more detail the effects of Pt in promoting Al₂O₃-scale formation; 2) systematically assess the effects of Hf content on the oxidation behavior of γ' and γ + γ' alloys; and 3) evaluate the performance of Pt+Hf-modified γ + γ' coatings.

Experimental Procedures

Bulk alloys were prepared at the Materials Preparation Center of the Ames Laboratory [12] by argon-arc melting the pure metallic constituents followed by drop casting into the form of 10 mm diameter rods. All as-cast rods were given an initial heat treatment in a flowing argon atmosphere at 1200°C for 6 hours followed by 1150°C for 48 hours. Disk-shaped (10 mm diameter by ~1 mm thick) test samples were then cut from heat-treated rods, polished to a 1200-grit surface finish and then cleaned in methanol and acetone.

Isothermal oxidation testing of the heat-treated alloys was conducted at 1150°C in air in order to gain insights into their intrinsic oxidation behavior. An open-ended horizontal tube furnace was used for these tests. Test samples were placed into an alumina tray in an inclined position in order to directly expose all sample surfaces to the air atmosphere. The sample tray was then slid into the hot zone of furnace, which was pre-heated to 1150°C, and then pulled out at the completion of the four-day test and allowed to air cool.

Both Pt-only and Pt+Hf-modified $\gamma+\gamma'$ coatings were deposited on a first-generation Ni-based superalloy substrate that contained nominally 1.5 wt.% Ti and no Hf or Y. For both coating types the first stage was to electroplate a $\sim 5\text{--}8\text{ }\mu\text{m}$ platinum layer onto the alloy surface. The Pt-only coating was prepared by a subsequent diffusion heat-treatment at 1080°C in vacuum for one hour. The Pt+Hf-modified $\gamma+\gamma'$ coating also involved a similar diffusion heat treatment that was then followed by co-depositing Al and Hf using a proprietary pack cementation process [13].

Cyclic oxidation testing of coatings and certain bulk alloys was conducted at 1150°C in ambient air within a vertical tube furnace having timer-controlled sample-extraction system. Each cycle consisted of one hour at 1150°C followed by 30 minutes at $\sim 75^\circ\text{C}$. Heating and cooling rates were approximately $200^\circ\text{C}/\text{minute}$. Weight-change measurements using an electronic analytical balance were made intermittently. No effort was made to retain any spalled scale. As a consequence, weight losses were sometimes recorded. The purpose of the cyclic test was to examine and compare the long-term performance of coatings and bulk alloys under the relatively aggressive conditions of thermal cycling (*i.e.*, generally more aggressive than isothermal testing).

Cross-sections of the oxidized samples were prepared using standard metallographic procedures. All oxidized samples were firstly electroplated with copper in order to separate the oxide scale from the epoxy mounting and, hence, improve edge retention of the metallographically polished cross-sections and reduce charging effects during electron microscope observations. The Cu-plated samples were then cold-mounted in a LECO long-cure epoxy. A Hitachi S-2460N secondary electron microscope (SEM) equipped with the energy dispersive spectrometer (EDS) was used to characterize the cross sections of the oxidized samples.

Results

Effects of Pt in Single-Phase γ and γ' Alloys

This part of the study focused on gaining a clearer understanding of the effects of Pt and Hf on the oxidation behavior of single-phase γ -Ni and γ' -Ni₃Al alloys. The alloy compositions studied are presented in Table 1. It is seen that binary γ -Ni and γ' -Ni₃Al alloys having a fixed nominal Al content of 12.5 and 25at.%, respectively, were prepared. Modifications of these alloys were also prepared by adding 10 or 20at.% Pt at the expense of Ni (*i.e.*, the Al contents were kept constant). The solubility limit of hafnium in γ is extremely low. As a consequence, 0.2 and 0.5at.% hafnium additions were made to only the γ' alloys.

Pt Effects in γ -Ni Alloys. Figure 1 shows cross sections of the oxide scales formed on single-phase γ -Ni alloys after four days isothermal oxidation in air at 1150°C . As shown in this figure, and based on the EDS results, the binary Ni-12.5Al alloy formed a three-layered scale structure comprised of an outermost NiO layer, an intermediate layer of NiAl₂O₄, and an innermost layer rich in Al₂O₃. The alloy/scale interface is seen to be non-planar. As can be inferred from Figure 1, the addition of Pt to the γ -Ni

Table 1. Nominal compositions (in at.%) of the single-phase alloys investigated.

Composition	Ni	Al	Pt	Hf	Phase
Ni-12.5Al	bal.	12.5	0	0	γ
Ni-12.5Al-10Pt	bal.	12.5	10	0	
Ni-12.5Al-20Pt	bal.	12.5	20	0	
Ni-25Al	bal.	25	0	0	γ'
Ni-25Al-0.2Hf	bal.	25	0	0.2	
Ni-25Al-0.5Hf	bal.	25	0	0.5	
Ni-25Al-10Pt	bal.	25	10	0	
Ni-25Al-10Pt-0.2Hf	bal.	25	10	0.2	
Ni-25Al-10Pt-0.5Hf	bal.	25	10	0.5	
Ni-25Al-20Pt	bal.	25	20	0	
Ni-25Al-20Pt-0.2Hf	bal.	25	20	0.2	
Ni-25Al-20Pt-0.5Hf	bal.	25	20	0.5

Figure 1. SEM images showing the cross sections of γ -Ni alloys after a four days isothermal oxidation at 1150°C in air.

alloy facilitated the primary formation of a more protective Al₂O₃ scale. The outward diffusion of Ni²⁺ through the scale was apparently hindered to the extent that no NiO was observed and only localized NiAl₂O₄ spinel was located at the scale surface on both the Ni-12.5Al-10Pt and Ni-12.5Al-20Pt alloys. The extent of NiAl₂O₄ formation decreased with increasing Pt content from 10 to 20at.%.

Figure 2 summarizes the measured thickness of each constituent layer in the oxide scale formed on each single-phase γ -Ni alloy. The thickness of the Al₂O₃ layers is seen to decrease from ~ 4.3 to $3.8\mu\text{m}$ with increasing Pt content from 10 to 20at.%.

Figure 2. Measured thicknesses of the constituent layers in the scales formed on γ -Ni alloys after four days at 1150°C in air: a) Ni-12.5Al; b) Ni-12.5Al-10Pt and c) Ni-12.5Al-20Pt.

Pt and Hf Effects in γ' -Ni₃Al Alloys. Cross sections of the oxide scales formed on single-phase γ' -Ni₃Al alloys after four days isothermal oxidation in air at 1150°C are shown in Figure 3. The benefit of Hf in reducing the rate of scale growth is clearly evidenced in this figure. In the case of Pt addition, it is seen by comparing the results in the vertical direction in Figure 3 that there are at least two beneficial effects. Firstly, and similar to what was found with the γ alloys, Pt addition promoted the exclusive formation of an Al₂O₃ scale. Secondly, the presence of Pt in the γ' alloy apparently decreased the reactivity of Hf, to the extent that HfO₂ formation could be suppressed (*N.B.*, under standard state conditions HfO₂ is thermodynamically more stable

than Al₂O₃ [14]). These effects are reported in more detail in the following.

The Ni-25Al alloy formed a planar $\sim 5\mu\text{m}$ Al₂O₃ scale with a discontinuous layer of NiAl₂O₄ at the scale surface after four days isothermal oxidation at 1150°C. This alloy also developed a subsurface layer ($\sim 8\mu\text{m}$) of γ -Ni owing to a greater amount of selective oxidation of Al relative to Ni. Addition of 10at.% Pt to the Ni-25Al alloy resulted in the exclusive formation of an Al₂O₃ scale, with a reduced overall scale thickness of $\sim 4.5\mu\text{m}$. Correspondingly, the depth of the subsurface, Al-depleted γ -Ni zone diminished to $\sim 3\mu\text{m}$. With even higher Pt content, *i.e.*, the Ni-25Al-20Pt alloy, a slightly thinner ($\sim 3.8\mu\text{m}$) exclusive Al₂O₃ scale formed. This scale also showed no evidence of spallation. In addition, no γ -Ni subsurface layer was observed in the alloy.

The Ni-25Al-0.2Hf alloy formed a mixed scale layer of Al₂O₃ and HfO₂ at 1150°C. This scale exhibited considerable spallation at the completion of oxidation. With the addition of 10at.% Pt to the alloy, *i.e.*, Ni-25Al-10Pt-0.2Hf, outer spinel formation was totally suppressed and the thickness of Al₂O₃ scale was decreased. Moreover, this scale showed no apparent spallation. Increasing the platinum content to 20at.% resulted in the formation of a homogeneous and continuous Al₂O₃ scale that was the thinnest observed and which showed no indication of spallation.

Figure 3. Cross-sectional SEM images of the various γ' -Ni₃Al alloys after four days isothermal oxidation at 1150°C in air.

The Pt-free Ni-25Al-0.5Hf alloy formed a complex and non-uniform oxide scale structure at 1150°C, consisting of a continuous layer of NiAl₂O₄ spinel above of a mixture of Al₂O₃ and HfO₂. There was also a discontinuous distribution of NiO at the scale surface as well as internal HfO₂ precipitates within the alloy subsurface. These precipitates were usually enveloped by Al₂O₃. However, 10at.% Pt addition to the Ni-25Al-0.5Hf alloy resulted in the development of a more planar Al₂O₃ oxide scale with the outer band of the scale containing small HfO₂ precipitates. There was no observable NiAl₂O₄. Increasing the platinum content to 20at.%, *i.e.*, the Ni-25Al-20Pt-0.5Hf alloy, resulted in the formation of an even thinner Al₂O₃ scale and a lesser amount of HfO₂ precipitates.

It is clear from the results in Figure 3 that the extent or even occurrence of HfO₂ formation was highly dependent on the presence and amount of platinum in the γ' alloy. In general, the preclusion of HfO₂ formation required a balance in Hf and Pt contents such that the Hf:Pt atom ratio needed to be below a certain value. Within the γ' composition space assessed in this study, that value is ~ 0.02 . It should be realized, however, that Hf over-doping, as manifested by unwanted HfO₂ formation, must eventually occur with increasing Hf content in a γ' alloy of a fixed Pt content.

Benefits of Pt for Increasing Scale Adhesion

In order to better understand the effects of Pt+Hf-modified $\gamma+\gamma'$ composition on oxidation behavior, six bulk alloys with relatively low Pt contents were investigated. The nominal compositions of these alloys are given in Table 2. All alloys were doped with 0.1at.% Hf. The Al content was fixed at either 15 or 20at.%, while the Pt contents increased from 0, 5 to 10at.%. The 15at.% Al alloys also contained 5at.% Cr in order to aid in promoting the formation and growth of an exclusive Al₂O₃ scale [11].

Table 2. Nominal compositions (in at.%) of low-Pt alloys studied.

Composition	Ni	Al	Pt	Hf	Cr
Ni-15Al-5Cr-0.1Hf	bal.	15	0	0.1	5
Ni-15Al-5Pt-5Cr-0.1Hf	bal.	15	5	0.1	5
Ni-15Al-10Pt-5Cr-0.1Hf	bal.	15	10	0.1	5
Ni-20Al-0.1Hf	bal.	20	0	0.1	0
Ni-20Al-5Pt-0.1Hf	bal.	20	5	0.1	0
Ni-20Al-10Pt-0.1Hf	bal.	20	10	0.1	0

Figure 4 shows the 1150°C cyclic oxidation weight change behavior of the various alloys for up to 500 cycles. The Pt-free, Ni-15Al-5Cr-0.1Hf alloy experienced an initial weight gain up to 90 cycles (0.6 mg/cm²), followed by extensive weight loss due to scale spallation. The addition 5at.% Pt to this alloy altered its oxidation behavior to the extent that it exhibited positive weight change throughout 500 cycles; although, the kinetics were rather linear and the final weight gain was about 1 mg/cm², which was the highest among the alloys tested. Increasing the Pt content in the Ni-15Al-5Cr-0.1Hf alloy to 10at.% caused a marked reduction in the oxidation kinetics, with the final weight gain being only about 0.4 mg/cm².

Figure 4. Weight-change kinetics of low-Pt alloys exposed to cyclic oxidation in air at 1150°C for up to 500 cycles.

Despite a slight weight loss in the latter stages of testing (*i.e.*, after ~ 320 cycles), the Ni-20Al-0.1Hf alloy performed much better than Ni-15Al-5Cr-0.1Hf. Platinum addition to the Ni-20Al-0.1Hf alloy resulted in slow rates of weight gain. The final weight change of Ni-20Al-10Pt-0.1Hf was less than half of what was gained on the Pt-free Ni-20Al-0.1Hf alloy after 500 cycles. The results from the cyclic oxidation tests clearly indicate that increasing Pt addition is beneficial to promoting the formation of an adherent and slow-growing scale.

Cross sections of the Ni-15Al-5Cr-0.1Hf-xPt ($x=0, 5$ and 10) alloys after 500 oxidation cycles at 1150°C are shown in Figure 5. Ni-15Al-5Cr-0.1Hf formed a duplex scale structure consisting of an outer layer of NiAl₂O₄ and an inner mixed layer of Al₂O₃ and HfO₂. There were also HfO₂ intrusions into the alloy at the alloy/scale boundary. The addition of 5at.% Pt to the Ni-15Al-5Cr-0.1Hf alloy resulted in the disappearance of the outer NiAl₂O₄ scale layer and the formation of a much thinner and more continuous Al₂O₃ scale. The amount of HfO₂ precipitation within the inner region of the scale was also greatly reduced. Further increasing the Pt content to 10at.%, *i.e.*, the Ni-15Al-10Pt-5Cr-0.1Hf alloy, led to the formation of an adherent, planar, slow-growing and continuous Al₂O₃ scale. It is thus clear that the presence of Pt can assist in the formation of a protective Al-rich oxide scale on a low-Al $\gamma+\gamma'$ alloy. Further, an important apparent aspect of the beneficial effects of Pt addition is to promote the scale adhesion.

Figure 6 shows the cross sections of Ni-20Al-0.1Hf-xPt ($x=0, 5, 10$) alloys after 500 oxidation cycles at 1150°C. A similar trend in the Pt effects as found for Ni-15Al-5Cr-0.1Hf-xPt alloys was observed for these former alloys. The Pt-free Ni-20Al-0.1Hf alloy formed a duplex scale structure comprised of NiAl₂O₄ at the surface followed in inner layer of Al₂O₃ containing HfO₂ precipitates. The addition of 5at.% Pt to the Ni-20Al-0.1Hf alloy led to the formation of a thinner and more continuous Al₂O₃ scale with localized NiAl₂O₄ at the scale surface. Further increasing the Pt content to 10at.%, *i.e.*, the Ni-20Al-10Pt-0.1Hf alloy, promoted the formation of a more homogeneous and planar Al₂O₃ scale, without any indication of HfO₂ precipitates within either the Al₂O₃ scale or the alloy subsurface.

Figure 5. Cross-sectional SEM images showing the scale formed on Ni-15Al-5Cr-0.1Hf-xPt ($x=0, 5$ and 10) alloys at 1150°C after 500 cycles.

The cyclic oxidation results obtained from these low-Pt ($<10\text{at.}\%$) alloys are deemed to be fairly good considering the relatively aggressive testing conditions of cyclic oxidation at 1150°C . It should be noted that the final weight gain on both the Ni-15Al-10Pt-5Cr-0.1Hf and the Ni-20Al-10Pt-0.1Hf alloys after 500 cycles was about one fourth that measured for a Ni-50Al-15Pt alloy ($\sim 1.52 \text{ mg/cm}^2$) exposed to the same oxidation testing conditions. Indeed, the current experimental results reveal potential for the use of Pt+Hf-modified $\gamma+\gamma'$ -based coatings in advanced TBC systems.

Pt+Hf-Modified $\gamma+\gamma'$ Coatings

Cyclic Oxidation Performance. Pt+Hf-modified $\gamma+\gamma'$ -based coatings were deposited on a first-generation Ni-based superalloy using a proprietary Al+Hf co-deposition pack cementation process [13]. For the purpose of comparison, a Pt-only coating on the same superalloy substrate and the bare superalloy substrate itself were also prepared for testing. Further, a Ni-50Al-15Pt alloy was chosen as a representative Pt-modified β -based composition for comparison; while bulk $\gamma+\gamma'$ alloys of composition Ni-20Al-20Pt and Ni-20Al-20Pt-0.3Hf were prepared for comparing the oxidation behavior to that of the coatings. The alloys and coatings were tested under cyclic oxidation conditions at 1150°C in air.

Figure 6. Cross-sectional SEM images showing the scale formed on Ni-20Al-0.1Hf-xPt ($x=0, 5$ and 10) alloys at 1150°C after 500 cycles.

Figure 7 shows the weight change of all tested samples through to 100 cycles at 1150°C . It is seen that the weight change of Ni-50Al-15Pt (0.57 mg/cm^2) alloy was about 0.6 times that of the Ni-20Al-20Pt (0.9 mg/cm^2) alloy after 100 cycles. However, and in accordance with the results presented earlier, 0.3at.% Hf addition to the Ni-20Al-20Pt alloy resulted in much reduced oxidation kinetics, with about a factor of two lower final weight change (0.32 mg/cm^2) after 100 cycles.

Figure 7. Weight-change kinetics of the coatings and alloys exposed to up to 100 thermal cycles at 1150°C in air.

It is seen in Figure 7 that the uncoated superalloy underwent a positive weight change during the first ~60 cycles, and thereafter exhibited a continuous weight loss. The Pt-only coating experienced an abrupt weight loss after only one thermal cycle, indicating that this coating was unable to form a protective oxide scale. In fact, this coating actually worsened the oxidation resistance of the alloy. By contrast, the Pt+Hf-modified $\gamma+\gamma'$ coating oxidized in a protective manner, with very low kinetics (final weight change was only $\sim 0.25 \text{ mg/cm}^2$) and no indication of scale spallation.

Figure 8 shows corresponding cross-sectional SEM images of the various samples tested through to 100 thermal cycles. It is seen that the thickness of the Al_2O_3 scale formed on Ni-50Al-15Pt was thinner than what formed on Ni-20Al-20Pt, which is in agreement with weight-change kinetics shown in Figure 7. In the case of the latter alloy, the selective oxidation of aluminum resulted in the formation of a $30\mu\text{m}$ -thick subsurface layer of γ -Ni. The addition of 0.3at.% Hf to the Ni-20Al-20Pt alloy caused a remarkable decrease in the Al_2O_3 -scale thickness. Correspondingly, the extent of aluminum removal was sufficiently low that a continuous subsurface layer of γ did not form.

The uncoated superalloy formed a two-layered scale structure comprised of an NiAl_2O_4 outer layer on an Al_2O_3 -rich inner layer. In addition, a $\sim 17\mu\text{m}$ thick subsurface layer of γ developed within the alloy. Since the Pt-only coating underwent continuous and extensive weight loss after the first oxidation cycle, its cross-sectional image was not very informative. This is because any aspect of the Pt-only coating was removed after the 100 thermal cycles. The Pt+Hf-modified $\gamma+\gamma'$ coating is seen to have formed a

thin and adherent Al_2O_3 scale without internal Hf oxidation. The non-planar surface of this coating was not a consequence of the cyclic-oxidation testing. Rather, the as-deposited coating structure was similarly non-planar. A further aspect of the Pt+Hf-modified $\gamma+\gamma'$ coating that can be inferred from Figure 8 is that it exhibited excellent phase compatibility with the Ni-based superalloy substrate, with no indication of unwanted SRZ formation.

Sensitivity of Coatings to Hf Content. The bulk-alloy results showed that the level of Hf must be limited in order to form a slow-growing and protective Al_2O_3 scale that is free of HfO_2 precipitates. This constraint must also extend to the Pt+Hf-modified $\gamma+\gamma'$ coatings; however, the influence of additional constituents in the coating that stem from the superalloy substrate may increase or decrease the propensity for HfO_2 formation. A comparison of the oxidation behavior of coatings with different as-deposited Hf levels is presented in Figure 9. Both coatings were oxidized in air at 1150°C for a total of 100 cycles. It is seen that the coating with an as-deposited Hf level less than 2at.% formed a planar and thin Al_2O_3 scale, with only localized internal HfO_2 precipitates near the scale/coating interface. By contrast, the other coating with an as-deposited Hf level greater than 2at.% formed a complex scale structure comprised of an outermost NiAl_2O_4 layer, an intermediate mixture of Al_2O_3 and HfO_2 , and a number of HfO_2 precipitates within the subsurface region of the coating. Clearly, for future Pt+Hf-modified $\gamma+\gamma'$ -based coating development it will be important to better understand the effects of Hf level and distribution on the oxidation behavior.

Figure 8. SEM images showing the cross sections of coatings and alloys after 100 oxidation cycles in air at 1150°C .

Figure 9. Cross-sectional SEM images of coatings with different as-deposited Hf levels that were oxidized at 1150°C in air for a total of 100 cycles.

Discussion

The current results showed that platinum addition to single-phase γ' -Ni₃Al and γ -Ni alloys can aid in promoting the selective oxidation of aluminum. The addition of 10at.% Pt to a Ni-12.5Al γ alloy caused the scale structure to change from triple-layered (NiO/NiAl₂O₄/Al₂O₃) to two-layered (NiAl₂O₄/Al₂O₃), as shown in Figure 1. Further increasing the Pt content to 20at.% resulted in a discontinuous outer layer of NiAl₂O₄ and a decrease in the thickness of the inner Al₂O₃ scale layer. In a similar yet more pronounced manner, 10at.% Pt addition to the Ni-25Al γ' alloy suppressed NiAl₂O₄ formation and promoted the exclusive growth of an Al₂O₃ scale, as shown in Figure 3. This alloy also formed a γ -Ni subsurface layer, which was due to the selective oxidation of Al leading to the $\gamma' \rightarrow \gamma$ transformation. The addition of 20at.% Pt to Ni-25Al promoted the formation of a thinner Al₂O₃ scale and the virtual absence of a γ -Ni subsurface layer.

The beneficial effects of Pt have been investigated in some detail by our group [8,10,11,15,16]. It has been shown that the so-called Pt-effect can be ascribed to a number of contributing factors. For instance, a first-principles study by Chao *et al.* [10] showed that Pt has a strong preference for the Ni lattice sites (face centers) in the ordered L1₂ structure of γ' -Ni₃Al at temperatures ranging from -273 to 1727°C. As a consequence, a given crystallographic plane of γ' containing both Al and Ni shows an increase in the Al:Ni atom fraction with increasing Pt addition. Such an effective Al enrichment at the γ' surface would kinetically favor the formation of Al₂O₃ relative to NiO. An important aspect of this inference is the non-reacting nature of Pt to oxidation.

Another contributing factor that was found in previous work is that the Pt-containing γ' -based alloys show subsurface Pt enrichment during the very early stages of oxidation [17]. This

enrichment would reduce Ni availability for oxidation and could also increase the Al supply to the evolving scale owing to the negative chemical interaction between Al and Pt. With regard to the latter, Pt decreases the chemical activity of Al [18], so that a subsurface Pt enrichment would confer an increased subsurface gradient in the Al activity and, hence, an increased Al flux from the alloy to the evolving scale. Such an effect would also contribute to kinetically enhancing Al₂O₃-scale formation.

Platinum was also shown to reduce or even preclude HfO₂ formation. This result indicates that Pt has a negative chemical effect on Hf, to the extent that the chemical activity (a_{Hf}) and hence reactivity of the latter is reduced. Thermodynamic considerations can help to elucidate the observed impact of Pt on the oxidation of Hf. At the testing temperature of 1150°C, HfO₂ is thermodynamically more stable than Al₂O₃ under standard state conditions [14]. Thus, Hf should always be oxidized below the Al₂O₃ scale as long as the Hf activity and content are above critical values. At dilute levels, the activity of Hf is directly proportional to the Hf content in accordance with Henry's law, *i.e.*,

$$a_{\text{Hf}} \approx \omega \times X_{\text{Hf}} \quad (1)$$

where ω is the activity coefficient and X_{Hf} is the Hf content. The internal oxidation of Hf may be represented by the following displacement reaction:

in which the underscoring indicates that the metal elements are in the alloy solution and therefore have chemical activities less than unity. The above reaction proceeds to the right in the Ni-25Al-0.5Hf alloy, as indicated in Figure 3. The thermodynamic criterion for this rightward progression is given by

$$\Delta G = RT \ln(K/K_{\text{eq}}) < 0 \quad (3)$$

where ΔG is the Gibbs free energy change for reaction (2), K is the reaction constant defined from the law of mass action by the activity quotient $(a_{\text{Al}})^4/(a_{\text{Hf}})^3$, K_{eq} is the equilibrium constant for which $\Delta G=0$, R is the gas constant and T is the absolute temperature. In the case of the Pt-modified Ni-25Al-0.5Hf alloys, no internal HfO₂ formation was observed, as seen in Figure 3. This leftward progression of reaction (2) requires that $\Delta G > 0$, which could have only occurred due to a significant decrease in the value of a_{Hf} . Since the Hf content in the alloys studied was relatively high (0.2 to 0.5at.%) from the standpoint of typical reactive element additions of the few hundreds ppm level, the above argument leads to the inference that the Hf activity in the alloys was decreased by the Pt additions, *i.e.*, Pt caused ω to be much less than unity. Furthermore, the extent of the Hf activity decrease is directly proportional to the Pt content, as was also reported elsewhere [19].

The present results also showed that Hf can significantly reduce the rate of Al₂O₃-scale growth, but only when it is added below a critical level, above which a negative effect arises in which non-protective HfO₂ forms. The reduction in Al₂O₃-scale growth rate with Hf added at a sub-critical level can be ascribed to a grain-blocking effect. As has been discussed by others [20], the growth of an alumina scale is predominated by grain-boundary diffusion.

Further, it is now well established that Hf cations tend to segregate to the grain boundaries of the alumina scale [21]. The resulting grain-boundary enrichment acts to impede the outward migration of Al (more than inward migration of O) to the extent that the growth rate of the Al_2O_3 scale is markedly reduced.

It was shown that Pt+Hf-modified $\gamma+\gamma'$ -based coatings are indeed protective alumina formers with improved high-temperature oxidation resistance. A major advantage in the application of these coatings is the absence of TCP and SRZ formations in the coating/superalloy interdiffusion zone. Due in part to the influence of other alloying elements, it was shown that coating performance can be highly sensitive to the Hf content compared to what was found from the bulk-alloy studies.

Summary

The influence of Pt and Hf additions on the high-temperature oxidation resistance of single-phase γ -Ni and γ' - Ni_3Al alloys were assessed by examining the thicknesses and structures of the thermally-grown scales. Platinum promoted Al_2O_3 formation by suppressing the NiO growth on both γ -Ni and γ' - Ni_3Al single-phase alloys. This effect increased with increasing Pt content and, in the case of γ' , can be partly attributed to the preference for Pt to occupy Ni lattice sites in the L_{12} crystal structure. It was deduced that Pt acts to reduce the chemical activity of Hf, to the extent that HfO_2 formation could be suppressed at a sufficiently high Pt content. Within the composition space that was studied, HfO_2 formation could be suppressed if the Hf:Pt atom ratio was below ~ 0.02 . Guided by the results from the bulk-alloy studies, a feasible method to deposit Pt+Hf-modified $\gamma+\gamma'$ coatings was developed. The oxidation resistance and stability of these coatings were found to be excellent when the Hf content was below ~ 2 at.%. Future work will focus on optimizing the coating compositions for resistance to both oxidation and hot corrosion.

Acknowledgement

The authors would like to acknowledge the support from the Office of Naval Research, with Dr. David Shifler being the program manager.

References

1. J.R. Nicholls, "Advances in Coating Design for High-Performance Gas Turbines," *MRS Bulletin*, September (2003), 659-670.
2. B. Gleeson, "Thermal Barrier Coatings for Aeroengine Applications," *Journal of Propulsion and Power*, 22 (2006), 375-383.
3. S. Bose, *High Temperature Coatings* (Butterworth-Heinemann, Burlington, MA, 2007) 155-232.
4. D.B. Miracle, "The Physical and Mechanical Properties of NiAl," *Acta Metallurgica et Materialia*, 41 (3) (1993), 649-684.
5. D.R. Clarke, C.G. Levi, "Materials Design for the Next Generation Thermal Barrier Coatings," *Annual Review of Materials Research*, 33 (2003), 383-417.
6. V.K. Tolpygo and D.R. Clarke, "Temperature and Cycle-Time Dependence of Rumpling in Platinum-Modified Diffusion Aluminide Coatings," *Scripta Materialia*, 57 (2007), 563-566.
7. W.S. Waltson, J.C. Schaeffer and W.H. Murphy, "A New Type of Microstructural Instability in Superalloys – SRZ," *Superalloys*, ed. R.D. Kissinger et al. (The Minerals, Metals & Materials Society, 1996), 9-18.
8. B. Gleeson, W. Wang, S. Hayashi, D. Sordet, "Effects of Platinum on the Interdiffusion and Oxidation Behavior of Ni-Al-Based Alloys," *Materials Science Forum*, 461-464 (2004), 213-222.
9. S. Hayashi, W. Wang, D.J. Sordet and B. Gleeson, "Interdiffusion Behavior of Pt-Modified γ -Ni+ γ' - Ni_3Al Alloys Coupled to Ni-Al-Based Alloys," *Metallurgical and Materials Transactions A*, 36A (2005), 1769-1775.
10. C. Jiang, D.J. Sordet, B. Gleeson, "Site Preference of Ternary Alloying Elements in Ni_3Al : A First-Principles Study," *Acta Materialia*, 54 (2006), 1147-1154.
11. T. Izumi, N. Mu, L. Zhang, B. Gleeson, "Effects of Targeted γ -Ni+ γ' - Ni_3Al -Based Coating Compositions on Oxidation Behavior," *Surface & Coatings Technology*, 202 (2007), 628-631.
12. Materials Preparation Center at the U.S. Department of Energy's Ames Laboratory; www.mpc.ameslab.gov.
13. B. Gleeson et al., US Patent, application: 20060127695, 2006.
14. D.R. Sigler, "Aluminum Oxide Adherence on Fe-Cr-Al Alloys Modified with Group IIIB, IVB, VB, and VIB Elements," *Oxidation of Metals*, 32 (5/6) (1989), 337-355.
15. S. Hayashi and B. Gleeson, "Effects of Pt on the Short-Term Oxidation Behavior of γ -Ni+ γ' - Ni_3Al Alloys," *Materials at High Temperatures*, 22 (3/4) (2005), 321-328.
16. F. Qin, C. Jiang, J.W. Anderegg, C.J. Jenks, B. Gleeson, D.J. Sordet, P.A. Thiel, "Segregation of Pt at Clean Surfaces of $(\text{Pt,Ni})_3\text{Al}$," *Surface Sciences*, 601 (2007), 376-380.
17. S. Hayashi, T. Narita, and B. Gleeson, "Early-Stage Oxidation Behavior of γ' - Ni_3Al -Based Alloys with and without Pt Addition," *Materials Science Forum*, 522-523 (2006), 229-238.
18. E. Copland, "Partial Thermodynamic Properties of γ' -(Ni,Pt) $_3\text{Al}$ in the Ni-Al-Pt System," *Journal of Phase Equilibrium and Diffusion*, 28 (1) (2007), 38-48.

19. T. Izumi and B. Gleeson, "Oxidation Behavior of Pt+Hf-Modified γ -Ni+ γ' -Ni₃Al Alloys," *Materials Science Forum*, 522-523 (2006), 221-228.
20. J.D. Kuenzly and D.L. Douglass, "The Oxidation Mechanism of Ni₃Al Containing Yttrium," *Oxidation of Metals*, 8 (3) (1974), 139-171.
21. W.D. Kingery, "Segregation Phenomena at Surfaces and at Grain Boundaries in Oxides and Carbides," *Solid State Ionics*, 12 (1984), 299-307.