Bond Coating Performance of Thermal Barrier Coatings for Industrial Gas Turbines

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Abstract

Thermal barrier coatings are intended to work in conjunction with internal cooling schemes to reduce the metal temperature of critical hot gas path components in gas turbine engines. The thermal resistance is typically provided by a 100 to 250 μm-thick layer of ceramic (most usually zirconia stabilized with an addition of 7-8 wt% of yttria), and this is deposited on to an approximately 50 μm-thick, metallic bond coating that is intended to anchor the ceramic to the metallic surface, to provide some degree of mechanical compliance, and to act as a reservoir of protective scale-forming elements (Al) to protect the underlying superalloy from high-temperature corrosion. A feature of importance to the durability of thermal barrier coatings is the early establishment of a continuous, protective oxide layer (preferably α-alumina) at the bond coating-ceramic interface. Since zirconia is permeable to oxygen, this oxide layer continues to grow during service. Some superalloys are inherently resistant to high-temperature oxidation, so that a separate bond coating may not be needed in those cases. Thermal barrier coatings have been in service in aeroengines for a number of years, and the use of this technology for increasing the durability and/or efficiency of industrial gas turbines is of significant interest currently. The data presented were taken from an investigation of routes to optimize bond coating performance, based on the premise that, ultimately, the weakest link in a thermal barrier coating system is the adherence of the protective oxide scale to the bond coating. The focus of the paper is on the influences of reactive elements and Pt on the oxidation behavior of NiAl-based alloys determined in studies using cast versions of bond coating compositions.

Key Words: Thermal barrier coatings; bond coatings; reactive elements; platinum additions; aluminum depletion effects.

Introduction

As part of a program in support of materials and manufacturing issues for the US Department of Energy's Advanced Turbine Systems program, a study was initiated to address longer-term issues based on developing a better understanding of the modes of degradation of thermal barrier coatings (TBCs) and by exploring routes whereby their performance could be improved and their service lifetimes increased. One of the complicating factors is that the properties and performance of TBCs can be very variable because of the different bond coating compositions and ceramic layer structures, as well as the variability inherent in the different processing routes used. Further, the details needed to develop an understanding of the reasons for the performance shortcomings in some cases are often proprietary. As a result, there was no common or agreed mode of degradation of TBCs that could provide a mechanistic basis for understanding the causes of performance degradation, hence there was no real basis to allow structured progress.

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One of the main goals of this study was to describe the actual mechanisms of degradation of TBCs to provide such a basis for improvement; incorporation into lifetime models would also improve their realism.

The overall premise that guided the effort was that when the processing variables for TBCs, especially for the ceramic layer, have been optimized, the weakest link in the TBC system will be the interface between the bond coating and thermally-grown oxide, and that this essentially will be independent of the ceramic layer used. As a result, the main focus of the effort was on maximizing the performance of bond coatings, although some issues involving the outer ceramic layer were addressed. The starting point was bond coating compositions based on β-NiAl using cast, model alloys. Comparison of the oxidation behavior of typical NiAl and NiCoCrAlY bond coating compositions had suggested that the aluminides had greater potential for providing oxidation protection at higher temperatures than did the MCrAlYs. The use of a 50 at% NiAl composition guaranteed that the alloy would reliably form the desired α-Al_2O_3 scale, and the use of cast model alloys removed complications arising from interdiffusion with a superalloy substrate, and from phase changes that can occur in an actual coating. Parallel studies were also carried out on aluminide coatings deposited on superalloys by chemical vapor deposition (CVD) [1]. The effectiveness of modifications resulting from the model alloy studies were evaluated to understand the influence of elements diffusing into the coating from the superalloy. The influence of the loss of Al by interdiffusion on phase change and coefficient of thermal expansion (CTE) change effects also were studied. The main tools used to evaluate the effectiveness of bond coating composition changes were oxidation testing using both isothermal and cyclic exposures to develop kinetic information, as well as post-exposure characterization using optical, scanning electron (SEM), and transmission electron microscopy (TEM), light-stimulated photoluminescence spectroscopy for measurement of stress and phase content of the alumina scales [1,2], as well as measurement of the CTE of various bond coating alloys [3]. Some of the oxidation exposures were conducted at temperatures up to 1200°C so as to accelerate the testing under conditions where the mechanisms of oxidation remained the same as at the expected service temperatures.

The issues addressed in the model bond coating alloy studies were:

- *Maximizing the oxidation lifetime* with emphasis on the effects of S, reactive elements (REs) such as Y and Hf on promoting the development of the desired scale, on the effects on its mode and rate of growth, and on its tendency to spall [4]. The effectiveness of different elements as single additions or as co-dopants was of particular interest, as was their interaction with impurities such as C. Similarly, the effectiveness of Pt, as well as alternative precious metals such as Ir, Pd, and Ru was examined [4,5], as was the influence of the initial surface finish of the bond coating on the ability to rapidly establish the desired α-Al_2O_3 scale.

- *Understanding the modes of degradation*, with particular focus on the implications of the loss of Al on the continued stability of a protective alumina scale, as well as on the phase stability and mechanical properties of the bond coating alloy. Studies involved determining the minimum Al level in Ni-Al castings for the continued stability of an α-Al_2O_3 scale, as well as the influence of REs and Pt on this minimum Al level.

- *Other concerns,* including the susceptibility of the bond coating compositions to hot corrosion resulting from exposure to impurities in the gas that would be expected in biomass-derived fuels [5,6], as well as the feasibility of developing a diffusion barrier to minimize Al loss and substrate element ingress to a bond coating based on β-NiAl [7].

Effects of Reactive Elements

One of the most widely-observed beneficial effects of RE additions is to improve the resistance of protective scales to spallation. The beneficial effect of removing S from the alloy on scale spallation behavior, in the absence of any RE addition, has been demonstrated [10], see for instance Fig. 1 [11]. Results suggest that Y additions in, for instance, NiCrAl alloys, can effectively inhibit the detrimental effects of S through the formation of stable sulfides [8], or by preventing S segregation at the interface between the substrate and the initial protective scale [9]. Reactive element additions also have a profound influence on the morphology of the protective oxide scale [4,9,12]. In alumina, they are segregated to the oxide grain boundaries where they significantly reduce the outward transport of Al, so reducing the rate of oxide growth which is now mostly by oxygen transport [9]. This change in predominant growth mechanism drastically changes the oxide morphology, and probably also contributes to improved scale adherence through

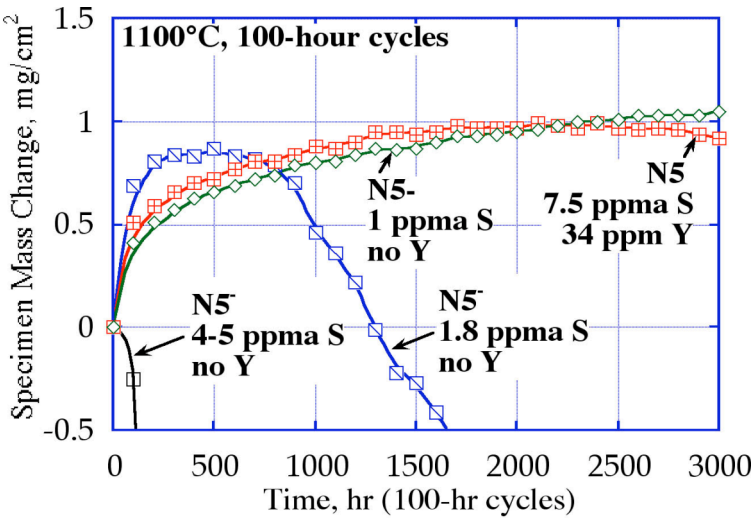

Figure 1. Effects of S and RE additions on the cyclic oxidation kinetics of a NiCrAl-based superalloy

the reduction of interfacial void formation since the flux of cation vacancies is reduced [12]. Comparison of SEM cross sections of alumina scales formed on undoped β-NiAl and Hf-doped β-NiAl (Fig. 2) illustrates these differences. With a Hf addition there are no alumina needles (formed by outward diffusion of Al), the scale has a columnar grain structure, and is thinner after the same exposure.

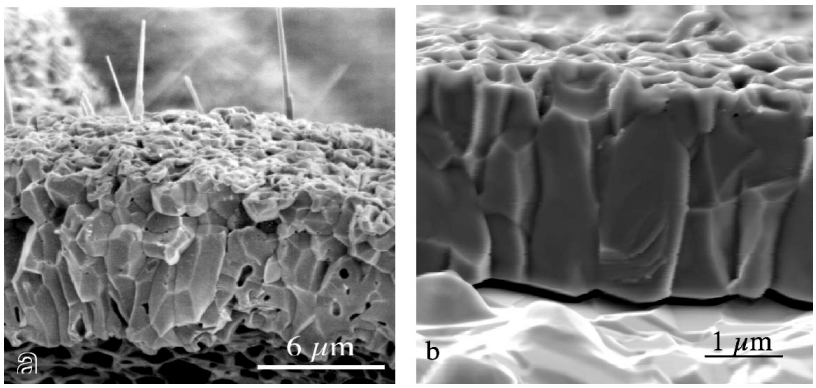

Figure 2. Cross sections of alumina scales formed after oxidation for 200h at 1200°C in air on (a) undoped β-NiAl, and (b) Hf-doped β-NiAl

The improved scale adherence, together with the reduction in oxidation rate resulting from RE doping, is illustrated by the oxidation kinetics shown in Fig. 3. These also indicate that

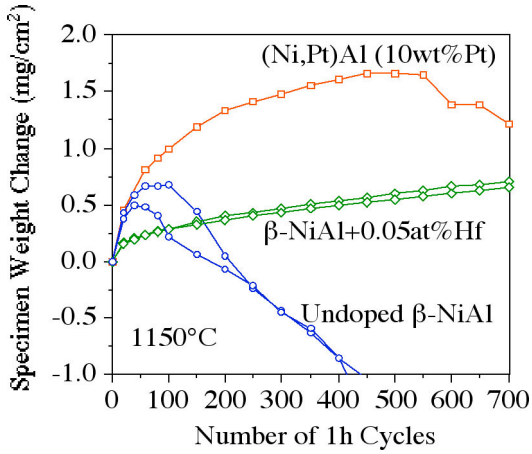

Figure 3. Influence of RE and Pt additions on the kinetics of cyclic oxidation of β-NiAl the addition of Pt to β-NiAl greatly improves the scale adherence, but does not affect the rate of oxide growth compared to the undoped alloy.

Practical Issues Concerning Reactive Element Additions

The beneficial effects of RE additions appear to depend on (a) having a sufficient amount of RE available, and (b) having a uniform distribution of the element in the coating [4]. The ability to satisfy these two requirements depends on the solid solubility of the RE in the coating. When RE additions in excess of the solubility limit are present, internal oxidation of the precipitated intermetallic particles occurs, and stringers of RE oxides are carried into the scale; both of these factors lead to an increase in oxidation rate, with some degradation of scale spallation resistance. Another factor is that some REs form stable compounds (e.g., Hf forms very stable carbides) that can significantly decrease the availability of the RE to participate in the oxidation reaction. In practice, it appears that Hf is the most effective in aluminides, where as Y gives better performance with NiCrAl alloys; the actual solubility levels of these REs are not known.

It is obviously difficult to meet these requirements easily in practical coatings, given that the optimum level of Hf in β-NiAl is of the order of 0.04 at% (approximately 0.28 wt%). One route that has been followed successfully in wrought and cast alloys has been the use of two or more RE additions each held at a level below its solubility limit in the alloy [13]. Examples are the wrought NiCrAl alloy Haynes 214, which is co-doped with 0.01 at% Zr and 0.003 at% Y, and the cast single crystal superalloy René N5, which contains 0.05 at% Hf, and 0.003 at% Y. While these are very small additions that must be accurately controlled, this is relatively easier in alloys made by melting and casting, than in coatings produced by processes such as CVD. Since there does not appear to be a RE with the effectiveness of Hf together with higher solubility in the high-Al NiAl coatings, other routes are needed for producing coatings with the optimized reactive element effect. Possible approaches include finding a bond coating structure (composition) with higher solubility for Hf, or the provision of a diffusion barrier between the bond coating and the superalloy substrate to prevent uncontrolled diffusion of elements such as Hf and Ti from the superalloy, and loss of Al from the coating. For a true diffusion barrier, all the elements required in the coating must be delivered by the coating process itself, rather than relying on Ni from the substrate as in CVD aluminizing.

Influence of Aluminum Level on the Bond Coating Properties

At the higher temperatures of operation, loss of Al from the aluminide coating by interdiffusion with the substrate becomes a major concern. In terms of bond coating life, the concern is that the coating Al content prematurely will fall below the minimum level required to avoid spinel formation. Equally important, however, is the effect of the influx of Al to the superalloy substrate on the solubility of refractory elements used for strengthening, resulting in precipitation of embrittling phases. A question addressed in this research was the minimum level of Al required to maintain a protective scale, that is, to prevent the formation of the $NiAl_2O_4$ spinel, and any influences exerted by Pt and RE additions.

The ability of an aluminide coating to form and maintain an α-Al_2O_3 scale is commonly considered to be lost when Al depletion results in the transformation of the β-phase to Ni_3Al (γ'). In some cases, a discontinuous β-phase can serve as an Al reservoir in a γ'matrix but, in general, Ni_3Al does not form the desired protective oxide scale. This is illustrated in Fig. 4, which shows protective oxidation behavior for Ni aluminides containing

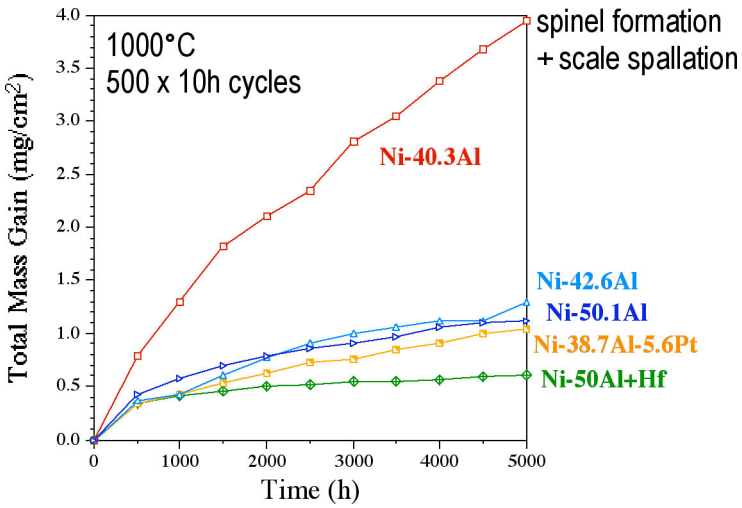

Figure 4. Influence of Al content on the cyclic oxidation kinetics (500-h cycles) at 1000°C

from 50 to 42.6 at% Al: the 40.3 at% Al alloy oxidized at a much faster oxidation rate due to the formation of the spinel. The total mass gain (equivalent to total oxygen uptake) also was increased in the Ni-40.3Al alloy due to increased scale spallation, which was minor for the other alloys. When Pt was added to a similar low Al content alloy, no spinel formation was observed. At the temperature of the test shown in Fig. 4, the available NiAl phase diagram [14] indicates that the lower limit of the β-phase is approximately 37 at% Al. Presumably, consumption of Al to form the initial oxide scale, followed by the scale spallation expected at each thermal cycle, was sufficient to deplete the surface Al content of the coating into the $\beta+\gamma'$ phase field.

Figure 5a shows oxidation kinetic data (represented as specimen mass change) at 1100°C under conditions where the specimens experienced 1-h thermal cycles. Note that all of the alloys were doped with Hf to minimize scale spallation. A trend to increasing oxidation rate with decreasing Al content was noted, together with the effectiveness of a Pt addition to a 37.6 at% Al alloy (the lower limit of the β phase field at 1100°C is approximately 36.5 at% Al). The Ni-34.7 Al-5.7 Pt alloy did not fit this trend, however, but exhibited a more rapid oxidation rate than the Pt-free version, and was found after oxidation to be severely deformed. Under conditions where the specimens experienced

thermal cycles at 100-h intervals (Fig. 5b), the behavior of this alloy was quite protective, and in fact its rate of oxidation was slower than the Pt-free counterpart. The topography of the Ni-34.7 Al-5.7 Pt alloy shown in Fig. 5b confirms its protective behavior in 100-h cycles, and provides a stark contrast with the specimen oxidized for the same total time but with more frequent thermal cycling (Fig. 5a).

Figure 6 indicates that under the more severe conditions of 1-h thermal cycles at 1200°C, the effect of Al and Pt were more clearly discriminated. The specimens with less than 37 at% Al (the lower Al limit of the β phase field at 1200°C is 34.9 at% Al) were heavily deformed, whereas specimens with higher Al levels showed no obvious deformation after 1000 cycles. The Pt-modified, hypo-stoichiometric alloy exhibited somewhat less deformation than the non-modified version, and maintained an alumina (grey) scale, whereas the Pt-free alloy developed a non-protective spinel (blue) that spalled. While the oxidation kinetics for the Pt-modified 37.6 at% Al alloy were similar to those for the non Pt-modified version, the former alloy nevertheless exhibited some scale spallation.

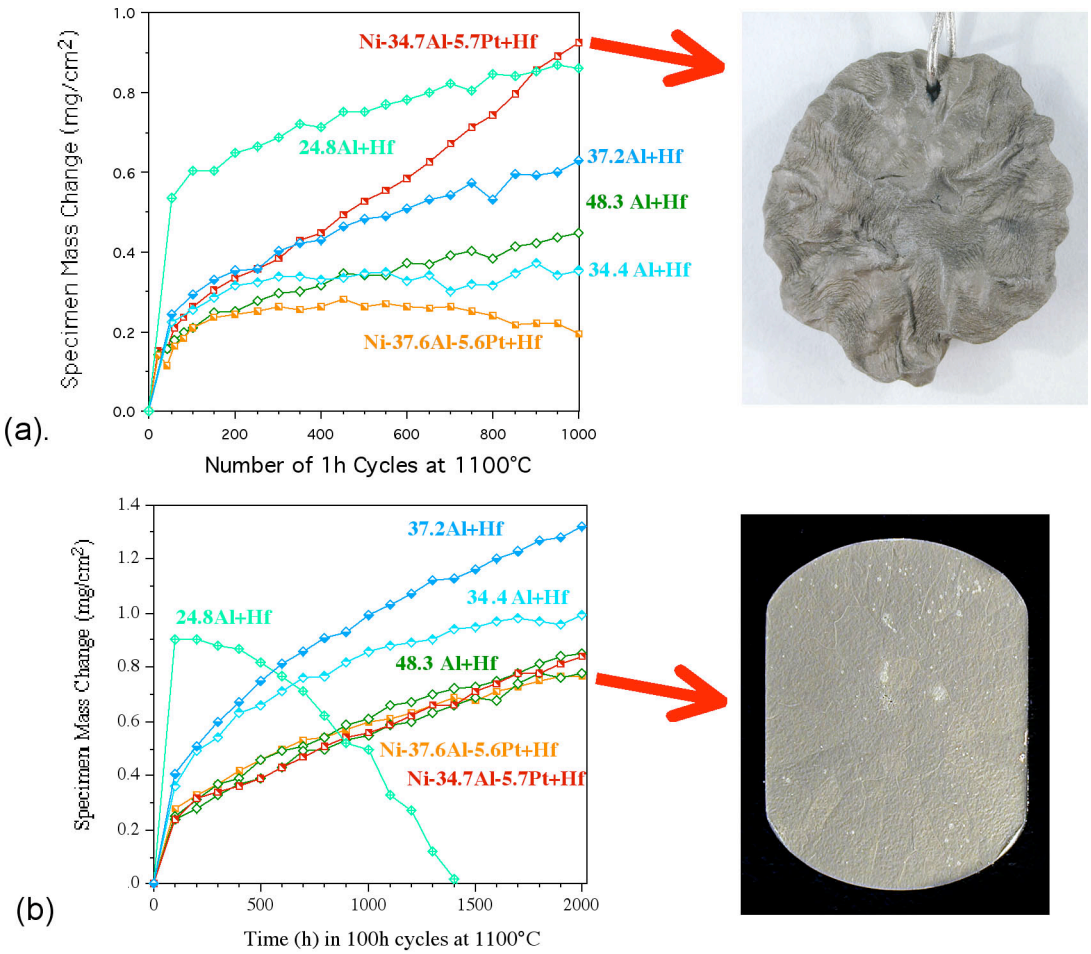

Figure 5. Effects of cycle frequency: (a) 1-h cycles and (b) 100-h cycles at 1100°C, on the oxidation kinetics and deformation of the hypo-stoichiometric aluminide. Macros of the Ni-34.7Al-5.7Pt+Hf alloy are shown for the respective conditions

These observations suggest that one possible source of stress that could drive this deformation could be repeated cycling between the β and (β+γ') phase fields, which involves a larger volume change than the 2% associated with the martensiic transformation [15]. Another is the difference between the CTE of the bond coating and superalloy substrate. As shown in Fig. 7, the ΔCTE with the superalloy René N5 was

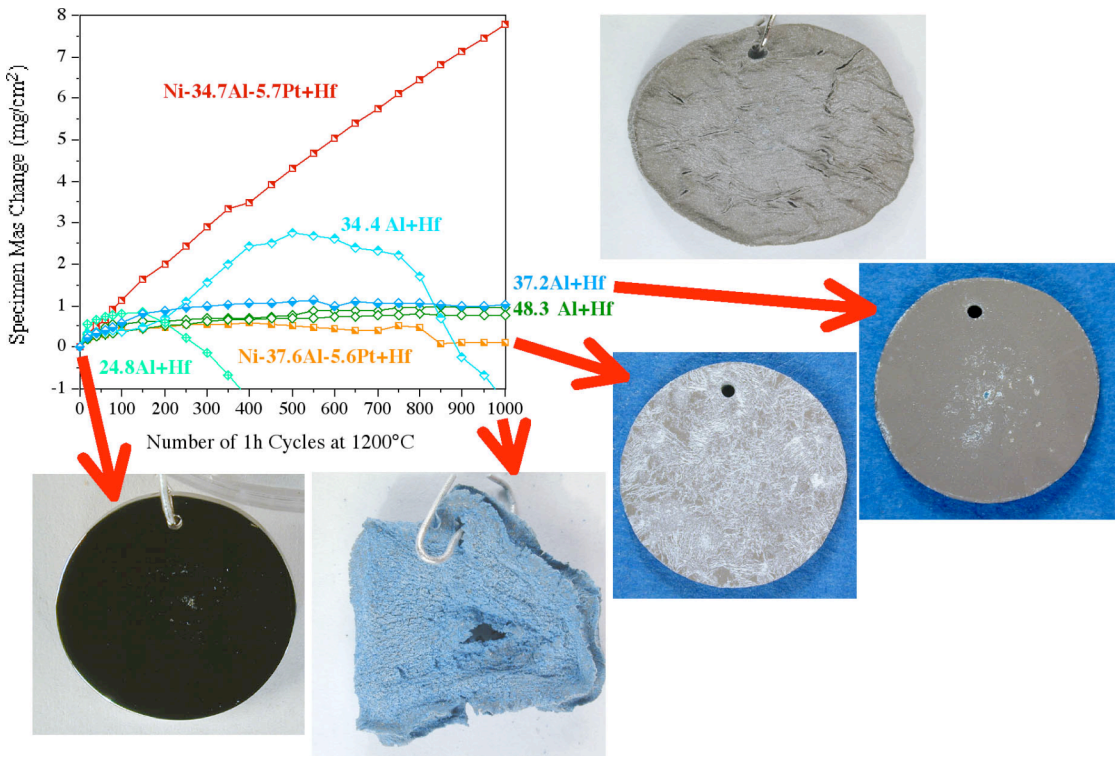

Figure 6. Cyclic oxidation behavior at 1200°C (1-h cycles)

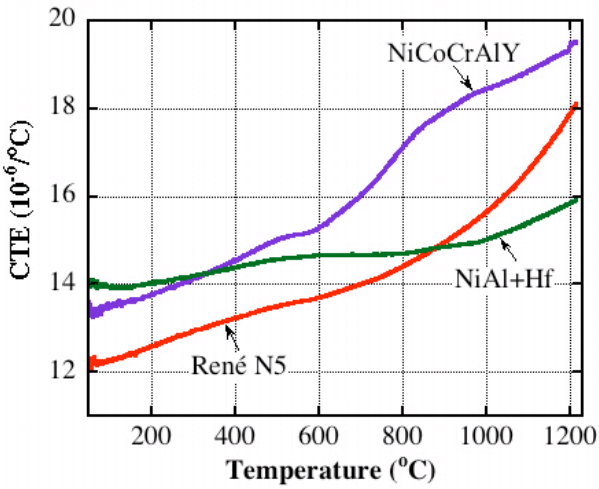

Fig. 7. Comparison of the temperature-dependence of the CTE of typical aluminide and MCrAlY bond coating alloys with that of superalloy René N5.

found to be lower for a Ni aluminide compared to a NiCoCrAlY bond coating composition at all temperatures above approximately 400°C. Further, the CTE for NiCoCrAlY was always greater than that for the superalloy, suggesting that such a bond coating would experience transient compressive creep on heating to temperature. The CTE of the aluminide matched that of the superalloy at approximately 850°C, and was lower at higher temperatures, suggesting that on heating to typical service temperatures such a bond coating would experience transient tensile creep.

Measured values of the CTEs of model NiAl and (Ni,Pt)Al bond coating compositions are shown in Fig. 8. Reducing the Al content of NiAl from 50.1 to 40 at% Al led to a minor

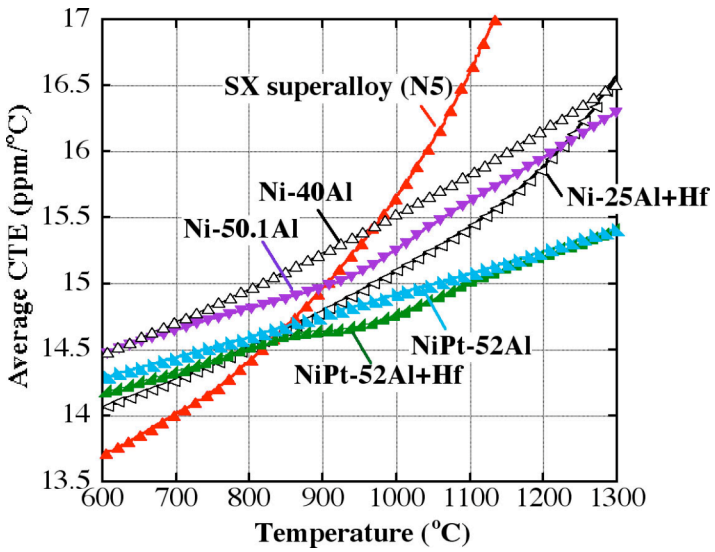

Figure 8. Temperature-dependence of the CTE of cast Ni-Al alloys

increase in CTE and slightly changed the shape of the temperature-dependence curve; further reduction to 25 at% Al (i.e., to Ni_3Al) lowered the CTE over the whole temperature range. Of particular interest is that an addition of 2.5 at% Pt lowered the CTE of Al-rich aluminides (52 at % Al), but had no effect on Ni-rich or stoichiometric β-NiAl (39-50 at% Al) [3]. RE additions had no effect on the CTE of the alloys studied.

Summary of the Role of Pt on Oxidation Behavior

Over the range of Pt additions studied, (0.1 to 5.2 at%, or 0.5 to 20 wt%), Pt was found to improve the resistance to scale spallation, apparently through the inhibition of interfacial void formation. On Pt-modified alloys, development of a protective α-Al_2O_3 scale was observed on alloys with Al contents as low as 38 at% at 1100°C, and 35 at% at 1200°C; this compares with 43 at% at 1000°C and 37 at% at 1100 and 1200°C for Pt-free alloys, and suggests that Pt improved selective oxidation to form alumina. Nevertheless, Pt additions in this range did not significantly modify the scale morphology, nor did they reduce the rate of growth of the oxide scale. Pt additions of 5.7 at% did not prevent deformation after cyclic oxidation of alloys with less than 37 at% Al. A Pt addition of 2.5 at% reduced the CTE of an Al-rich alloy (52 at% Al) but had no effect at lower Al contents (50-39 at%). Observations from coating studies [16] suggested that Pt remarkably increases the tolerance of aluminide coatings to S in the superalloy substrate, such that coatings formed on high-S superalloys formed protective oxide scales with no sign of detrimental effects of S-segregation at the oxide-bond coat interface. In those studies, Pt-modified aluminides did not appear to provide any change in the rate of ingress of refractory metals or decrease the rate of Al back-diffusion into the substrate compared to Pt-free aluminide coatings.

Overall Summary

A major point arising from studies of cast model alloys representing aluminide bond coating compositions is that RE additions to aluminides can lead to a very significant increase in their oxidation lifetimes through reduction in the rate of oxidation and increased resistance to scale spallation. However, the specifications for realizing these effects are difficult to attain in β-NiAl-type diffusion coatings. Possible routes might include better matching of the solubility of the REs in the bond coating alloy, possibly by co-doping

approaches, or by the provision of a bond coating-substrate diffusion barrier. Platinum additions up to 5.7 at% (20 wt%) were found to confer benefits of improved resistance to scale spallation, possibly associated with an observed increased tolerance to S, as well as the selective formation of an alumina scale (as opposed to a spinel scale) at lower levels of Al in the bond coating than in Pt-free alloys. It was found that, with decreasing Al content in model bond coating alloys, a point was reached where very significant deformation of the alloy occurred after cyclic oxidation exposures. The extent of deformation increased with increasing cycle frequency. Such deformation was presumably the result of repeated changes in phase in the bond coating (between β at high temperature and $\beta+\gamma'$ at low temperature) that occurred over the temperature range of interest. Platinum additions did not prevent such deformation, but were of benefit because of the maintenance of a protective alumina scale on the deformed surfaces.

Acknowledgements

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