Formation of Low Growth Rate, Highly Adherent Thermally-Grown Oxides for Prime Reliant Thermal Barrier Coating Systems

Abstract

Thermal barrier coating (TBC) systems, needed for higher thrust with increased efficiency in gas turbines, typically consist of an alumina-forming alloy or intermetallic bond coat and a ceramic topcoat. The durability and reliability of TBC systems are critically linked to the oxidation behavior of the bond coat. Ideally, the bond coat should oxidize to form a slow-growing, non-porous and adherent thermally grown oxide (TGO) scale layer of α-Al_2O_3. The ability to promote such ideal TGO formation depends critically on the composition and microstructure of the bond coat, together with the presence of minor elements (metal and non-metal) that with time diffuse into the coating from the substrate during service. An experimental program will be undertaken to attain a more detailed fundamental understanding of the influences of alloy/bond coat composition, microstructure, and surface condition (*i.e.*, in the as-received "bare" state or pre-oxidized before service) on TGO adhesion/cohesion and mechanical integrity. A range of NiCoCrAlY and NiAl-Pt alloy and coating formulations will be studied. The formation, growth and spallation behavior of TGO scales from these formulations during isothermal and thermal cycling tests at 950-1200°C will be studied, together with the extents and behavior of coating/substrate interdiffusion. The adherence and integrity of the TGO scales will be quantified by determining time- and composition-dependent mechanical parameters, such as interfacial fracture toughness. The fundamental understanding gained from this chemically-oriented program will provide an improved technical base for the development of a truly prime reliant TBC system that is necessary to meet longer-term defense-related and commercial goals. Moreover, a chemical approach, as opposed to a mechanical approach, provides the most practical foundation for life-prediction modeling of TBC systems.

The proposed program consists of a five-member, multidisciplinary research team from Iowa State University, and collaborative interactions with Rolls-Royce Allison, NASA Glenn Research Center, and Oak Ridge National Laboratory. The program is heavily focused on student training, with the proposed involvement of 9 PhD students, 10 Masters students, and numerous undergraduate students.

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1. Introduction

The demand for improved performance in high-temperature mechanical systems has led to increasingly severe operating environments, particularly for the components in advanced gas-turbine engines. Future improvements in gas-turbine performance will require even higher operating efficiencies, longer operating lifetimes, and reduced emissions. Achieving these requirements will necessitate still further increases in the gas inlet temperatures and, consequently, the development of structural materials possessing inherently higher temperature performance. Advanced cooling schemes coupled with thermal barrier coatings (TBCs) can enable the current families of nickel-base superalloys to meet the materials needs for the engines of tomorrow. Thermal barrier coating systems are currently capable of providing metal temperature reductions of up to about 140°C, while potential benefits are estimated to be greater than 170°C. However, as indicated in a recent National Research Council report [1], lack of reliability, more than any other design factor, has handicapped prime reliance acceptance of TBC systems for gas turbines.

Commercial advanced TBC systems are typically two-layered, consisting of a ceramic topcoat and an underlying metallic bond coat. The topcoat, which is usually applied either by air plasma spraying (APS) or electron beam-physical vapor deposition (EB-PVD), is most often yttria-stabilized zirconia (YSZ). The properties of YSZ are such that it has a low thermal conductivity, high oxygen permeability, and a relatively high coefficient of thermal expansion. The YSZ topcoat is also made “strain tolerant” by depositing a structure that contains numerous pores and/or pathways. The consequently high oxygen permeability of the YSZ topcoat imposes the constraint that the metallic bond coat must be resistant to oxidation attack. Thus, the bond coat is rich in aluminum to form a protective, thermally grown oxide (TGO) scale of α-Al_2O_3. In addition to imparting oxidation resistance, the TGO serves to bond the ceramic topcoat to the substrate/bond coat system. Notwithstanding, it is generally found that spallation and/or cracking of the thickening TGO scale is the ultimate failure mechanism of commercial TBCs, particularly EB-PVD TBCs [2-4]. Thus, improving the adhesion and integrity of the interfacial TGO scale is critical to the development of more reliable TBCs.

The adhesion and mechanical integrity of the TGO scale is very dependent upon the composition and structure of the bond coat. The bond coat is typically either an MCrAlY overlay (where M=Ni,Co, or both) or a platinum-modified diffusion aluminide (β-NiAl-Pt). The composition and phase constitutions of such bond coats vary. For example, NiCoCrAlY overlay coatings mainly consist of γ-Ni and β-NiAl plus, depending on temperature and coating composition, additional phases such as γ'-Ni_3Al, α-Cr, and σ-(Co,Cr). Both the MCrAlY and NiAl-Pt types of coating were originally developed to enhance long-term oxidation and corrosion protection of turbine components rather than specifically as bond coats. The oxidation resistance provided by these coatings allowed alloy developers to maximize the high-temperature mechanical properties of nickel-base superalloys. The original coatings required a high aluminum content in order to ensure re-healing of the Al_2O_3 scale after repeated spalling during service. In the case of TBC systems, however, Al_2O_3 healing after scale spallation is not an important requirement for ceramic adhesion. This is because the adhesion, and therefore the reliability, of a TBC system is dictated primarily by the first spallation event of the TGO scale.

As a consequence, the currently used bond coats, which were originally designed for Al_2O_3 re-healing capability, do not necessarily possess optimum compositions and/or structures for prime reliant TBC systems. Gaining a more detailed understanding of the interrelationships between bond-coat-scaling behavior and bond-coat composition and structure is integral to the further improvement of TBC durability and reliability. Moreover, the information gained from such an understanding is necessary before for accurate quantitative modeling of TBC performance can be achieved.

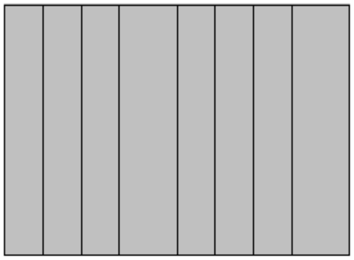
The importance of the TGO to the overall longevity and performance of a TBC system is well established. However, studies to understand and ultimately improve TBC performance have hitherto been significantly biased to the mechanical aspects associated with the TGO rather than the chemical aspects. As a consequence, there are many deficiencies and idealized assumptions in the present understanding of the science underpinning prime reliant coatings.

Current life-prediction models [5,6] describing TBC failure by thermal fatigue simply account for bond-coat oxidation by introducing a critical TGO thickness. This critical thickness is usually taken to be about 10 μm for an APS YSZ coating and 4-7 μm for an EB-PVD coating, and it is assumed that at a thickness greater than the critical value the TGO becomes prone to spallation, thereby deteriorating TBC lifetime. In addition to thickness, the tendency for a TGO to spall during the practical situation of thermal cycling depends on such factors as: temperature change (ΔT); minimum temperature during the cycle; severity of thermal transients/gradients; difference in coefficient of thermal expansion (ΔCTE) between the TGO and the bond coat/substrate system; the mechanical properties of the TGO and the bond coat; and the strength of adhesion at the TGO/bond coat interface. It is noted that, for a given application, many of these factors are fixed, such as the temperature change and the severity of the thermal transients and gradients. Similarly, some of the properties of the coating system are relatively fixed. For example, the TGO scale is generally considered to be quite stiff and strong, even though the scale structure may vary. Time-dependent factors associated with the scale include its growth rate, adherence, and TGO/bond coat interfacial structure and composition. Related to these factors are the homogeneity, composition, and structure of the TGO and bond coat, and the presence of physical defects (*e.g.*, voids and microcracks) in the TGO and/or the TGO/bond coat interface [7,8]. All of these variables are associated with chemical and structural effects, which are the main focus of the currently proposed study.

The importance of chemical and structural effects on the TGO properties and, in turn, on TBC performance is clearly shown in recent results from work with model TBC systems [7,9]. For example, Pint *et al.* [7] showed that the time to failure of an EB-PVD YSZ topcoat applied to an NiAl+400 ppma Zr bulk alloy, which forms a slow-growing, strongly adherent alumina scale, was extended by more than fourfold in comparison to a similar topcoat applied to a Y-doped superalloy plus state-of-the-art bond coat combination. Thus, improving TGO adherence and integrity directly leads to a significant increase in TBC life. The same study by Pint *et al.* also showed that the chemistry of the superalloy has a strong effect on TBC lifetime, with desulfurization being beneficial and the combination of desulfurization plus minor yttrium addition being even more beneficial. The results clearly show that for maximum TBC lifetime, the optimum bond coat composition and structure must also minimize the effect of deleterious elements, such as sulfur (an indigenous impurity), diffusing from the superalloy. (Note that yttrium is difficult to homogeneously incorporate in an alloy at the trace levels required (*i.e.*, <0.1 wt.%) and removal of sulfur content down to the extremely low levels necessary to have no harmful effect (*i.e.*, <0.5 ppm) is very costly and even not practicable for some alloys.)

Model alloys (*e.g.*, aluminum-rich β-NiAl with a minor addition of Zr or Hf) that are known to form an "ideal" alumina scale are generally not suitable for commercial TBC systems. This is because oxidation resistance is not the sole consideration; corrosion resistance of the bond coat and its compatibility with the substrate, together with physical and mechanical properties, are also concerns. Varying the substrate and bond coat compositions and microstructures to address these concerns will affect the properties of the TGO which, in turn, will affect the service life of the TBC system [8]. *In order to further develop TBC systems having increased reliability and durability, it is imperatively necessary to gain a more complete understanding of the oxidative effects of composition, microstructure and surface condition (i.e., 'bare" or pre-oxidized) of both relevant bond coat formulations and state-of-the-art nickel base alloys.* With regard to the latter, it is worth noting that, unlike the polycrystalline and the directionally-solidified alloys of the past, the current single-crystal nickel-base superalloys contain sufficient concentration of aluminum (~5-6 wt.%) to form Al_2O_3. Indeed, the potential exists to modify the state-of-the-art nickel-base superalloys so that they do not require a bond coat as it presently exists. Removal of the need for the relatively thick bond coat would offer the advantages of reducing component weight and cost. Figure 1 schematically compares a current advanced TBC system with a hypothetical ideal system of the future in which the bond coat is replaced by a comparatively thin surface region of the alloy that has been chemically and/or structurally modified for rapid establishment and sustained growth of an optimum TGO. Before this ideal TBC system can be realized, it is first necessary to firmly establish the chemical and structural factors affecting the formation, adhesion and mechanical integrity of a thermally grown alumina scale. The specific factors of concern in the currently-proposed study are phase constitution of NiCoCrAlY and NiAl-Pt alloys (*i.e.*, β, β+γ, β+ γ′, γ+ γ′), distribution and volume fraction of phases in a given multiphase alloy, the presence of minor elements in the alloys (*e.g.*, S, Ti, Re, Hf, Y), and pre-oxidation under different controlled conditions to promote exclusive α-Al_2O_3 scale formation. Optimization of these chemical and structural factors is required before useful and effective life-prediction models can be developed.

In assessing a given bond coat system, it is also important to realize that its composition and structure change with time in service due to both TGO-scale growth and interdiffusion with the substrate. The occurrence of coating/substrate interdiffusion decreases the concentration of aluminum in the coating, thereby reducing the ability of the coating to sustain exclusive Al_2O_3-scale growth, particularly in the event of localized detachment and/or microcracking, and introduces unwanted elements (*e.g.*, sulfur and titanium) which can promote oxide-scale spallation [10]. A further consequence of coating/substrate interdiffusion, particularly for the next generation of superalloys with up to 6 wt.% rhenium, is the formation of topologically close-packed (TCP) phases in the region of the original coating/substrate interface which can be deleterious to the mechanical properties of the superalloy substrate.



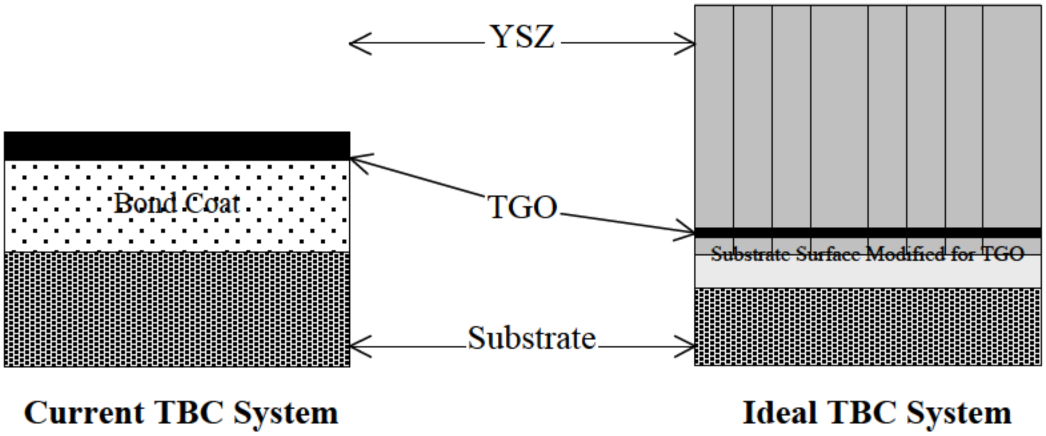


Figure 1 *Schematic comparison between a current state-of-the-art TBC system and the longer-term ideal, bond-coat free TBC system.*

It is to be expected that as the operating temperature of the turbine increases, so will the extent of coating/substrate interdiffusion. The extent of interdiffusion is dependent on the bond coat and substrate compositions, temperature, and time at that temperature. Gaining a better understanding of these dependencies would aid greatly in the selection of optimum bond coat/substrate systems for improved TBC performance and, hence, extended component life. Moreover, the ability to quantify rates of interdiffusion, particularly of the elements known to be detrimental to TGO adherence and integrity (*e.g.*, S and Ti), provides an alternative yet viable method for predicting TBC lifetime. The method envisioned is based upon determination of the time necessary to reach a critical concentration of a particular detrimental element at the TGO/alloy interface.

In summary, the durability and reliability of advanced TBC systems are critically linked to the oxidation behavior of the bond coat. Ideally, the bond coat should oxidize to form a slow-growing, non-porous and adherent α-Al_2O_3 scale layer. The ability to promote such ideal TGO formation requires a sound understanding of the influence of bond coat composition, microstructure and surface condition at all stages (*i.e.*, very early to long term) of the TGO-formation process. Associated with this are the oxidative effects of minor elements (metal and non-metal) that with time diffuse into the coating from the substrate during service. Gaining an understanding of these different chemical and structural factors will provide an improved technical base for the development of a truly prime reliant TBC system that is necessary to meet longer-term defense-related and commercial goals.

2. Principal Aim and Objectives of Proposed Study

The principal aim of the proposed novel study is to gain a more detailed fundamental understanding of the influences of alloy composition, microstructure, and surface condition (*i.e.*, in the as-received "bare" state or pre-oxidized before service) on the adhesion/spallation resistance of TGO scales for the purpose of improving the reliability and durability of advanced

TBC systems. An experimental approach will be taken initially, from which the important chemical and structural factors governing TGO growth and adhesion will be determined. A range of alloy/coating compositions and phase constitutions will be examined, with emphasis placed on the role of platinum, an element well known to play a dominant role in Ni-Al systems. Key, composition-dependent mechanical parameters will be determined in order to provide a relative quantitative assessment of the various compositional and structural effects. The important information gained from these measurements will also be useful for the development of accurate life-prediction models of TBC systems. Stated below are the principal objectives of the proposed study. The objectives are collectively broad in scope; they are, however, all aimed at understanding TGO growth behavior and adhesion for improved TBC performance. The breadth of the objectives reflects the complexity of advanced TBC systems and the need to focus initially on a number of important aspects.

The principal objectives are as follows:

(i) Determine the chemical and structural factors governing the exclusive formation of a thin, non-porous and adherent α-Al_2O_3-scale layer on different NiCoCrAlY and NiAl-Pt alloy and coating formulations. Emphasis will be placed on (a) the establishment of a homogeneous α-Al_2O_3 scale, (b) the rates of scale growth, (c) modes of oxidation, and (d) the effectiveness of the scales in maintaining protection during long-term thermal-cycling exposures.

(ii) Determine optimum platinum-modified aluminide coating compositions and structures for improved high-temperature oxidation resistance, and deposit selected coating compositions via the vacuum plasma spray process.

(iii) Determine the effects of bond coat and substrate compositions on the kinetics and behavior of coating/substrate interdiffusion, with the results used to further understand and develop an existing diffusion model. Of particular interest are the rates of minor-element diffusion and the interfacial contents of those elements that cause deterioration in scaling behavior.

(iv) Determine relative composition- and time-dependent mechanical parameters (*e.g.*, fracture toughness of the TGO and the TGO/alloy interface) in order to quantify the various chemical and structural effects and also to provide useful input data for life-prediction models of TBC systems.

The results from this study will provide a sound technical base for the development of substrate/bond coat systems, as well as novel surface-modified substrates that do not require a bond coat per se, that ensure TBC reliability and durability.

An important impact of the proposed study is improved component performance in high-temperature mechanical systems, particularly in gas turbines. Associated with this is an increase in the ability to meet the demand for reliable coatings that possess predictable failure mechanisms and extend the operating range of applications. All of these impacts are of direct relevance to defense missions requiring high-performance, high-temperature materials.

3. Technical Background

This section provides a brief technical background to the various important aspects associated with the objectives of the proposed study. The information that is provided in this section supports the research plan outlined in the subsequent section.

3.1 The Nature and Stages of TGO Development

There has been much research into the formation and growth of protective α-Al_2O_3 scales [11-13]. Establishment of an Al_2O_3-rich scale requires the alloy to contain more than a critical content of aluminum, which depends on the concentrations of the other alloying elements, the structure of the alloy and the oxidation conditions, particularly temperature and oxygen partial pressure. Establishment of an α-Al_2O_3 scale at temperatures below about 1100°C is especially complicated by the fact that there are several cubic or transitional Al_2O_3 structures, such as γ, δ and θ, that form during the transient stage of oxidation. The metastable, transitional Al_2O_3 structures grow at a faster rate than α-Al_2O_3 and often grow as blades or whiskers [11]. The growth of the metastable phases during the transient stage of oxidation can influence considerably the overall amount of oxidation and the subsequent growth of the stable α-Al_2O_3 phase. For example, eventual transformation of metastable θ-Al_2O_3 to the stable α-Al_2O_3 produces an 8-13% volume reduction which results in apparent tensile stresses in the scale [14] and scale cracking [15]. The effect of Al_2O_3 transformation on the performance of TBC systems has not been systematically investigated. It has been shown empirically, however, that pre-oxidation of the bond coat to stabilize the α-Al_2O_3 scale significantly improves the lifetime of a TBC system [16,17].

The effects of minor elements in the alloy on the rates of Al_2O_3 transformation to the stable α structure are unclear; there is, however, evidence to suggest that Cr [18], Ti [19] and Pt [20] can exert an accelerating effect on the transformation. Water vapor and oxygen partial pressure in the atmosphere can also influence the transformation rate and may even promote exclusive α-Al_2O_3 formation [11]. Moreover, the oxidation behavior of a continuous and adherent α-Al_2O_3 scale does not seem to depend on water vapor content in the oxidizing atmosphere [21]. By contrast, spallation of a moderately adherent α-Al_2O_3-rich scale is exacerbated in the presence of water vapor [22].

The establishment of a protective TGO scale on an initially "bare" alloy surface during isothermal oxidation can be generally characterized as involving three stages: a transient stage, followed by a steady-state stage, and finally a breakaway stage. Virtually all thermodynamically stable oxides can form during the transient stage, depending on the alloy system, oxidizing atmosphere and temperature. The duration of the transient stage may be seconds or days. The steady-state stage commences when the long-term phase constitution of the scale is established. The breakaway stage corresponds to failure of the steady-state scale and the subsequent formation of less-protective oxides. As TBC failure typically would occur before the onset of the breakaway stage, breakaway will be considered in this study only to the extent that its occurrence must be prolonged beyond the useful lifetime of the TBC system.

The transient stage of oxidation is particularly important in TBC systems because bond coats are often multiphase, with the different phases often having large differences in aluminum content. Initial high-temperature exposure of these multiphase materials to air typically results in the formation of a transient, heterogeneous scale, consisting of different oxides (*e.g.*, stable and metastable Al_2O_3, Cr_2O_3, $NiCr_2O_4$, etc) nucleating to varying extents on the different phases [23]. (Though less significant, the formation of a heterogeneous, transient-oxide scale will also occur on single-phase coatings.) Eventually, α-Al_2O_3 becomes the dominant oxide in the TGO, however the stresses resulting from the continuance and/or transformation of the previously established transient oxides can adversely affect the life of the TBC system. Further, the amount and distribution of impurities in the Al_2O_3 which eventually develops can differ between the metallic phases [8]. The variability in α-Al_2O_3 formation behavior with metallic phase constitution and oxidizing conditions is of great importance to the optimization of TBC systems.

The chemistry of the alloy surface prior to high-temperature exposure is another important, but little studied, factor affecting the transient stage of oxidation. It is generally found that the ratio of metallic elements in the passive layer that develops on the surface of a given alloy at room temperature is different from the corresponding ratio in the bulk alloy [24,25]. For instance, Ahmad and Fox [24] recently showed that a commercial (in wt.%) Ni-20Cr-1.3Si-0.4Mn-0.2Al alloy forms a passive oxide layer at room temperature that is rich in Al and Si. The passive layer was purported to have suppressed the formation of either NiO or $NiCr_2O_4$ and to have facilitated the relatively rapid establishment of a protective Cr_2O_3 scale. With regard to Al_2O_3-scale formation, several studies have reported the use of surface-sensitive techniques to characterize the interaction of NiAl alloy surfaces with oxygen [26-28]. Although the systems and oxidizing conditions studied were not directly relevant to bond coats for commercial TBC systems, the results do highlight the usefulness of advanced surface analysis for gaining a better understanding of the processes involved in the transient stage of oxidation. For example, Young *et al.* [26] showed using X-ray photoelectron spectroscopy (XPS) that stoichiometric, polycrystalline samples of NiAl form a nickel-containing Al_2O_3 scale when directly inserted into a furnace at 600°C under atmospheric pressure of O_2, but form an Al_2O_3 scale without any detectable Ni when pre-heated to 600°C in vacuum ($5x10^{-7}$ mbar) before exposure to O_2. By closely examining the binding energy peak positions of the $Ni2p_{3/2}$ photoelectrons, it was possible to show that, in the former case, the Ni was present as a spinel ($NiAl_2O_4$) rather than as the single oxide (NiO). The use of XPS is further strengthened when used in conjunction with low energy ion scattering (LEIS) spectroscopy, as it is possible to determine both the composition of the growing transient oxide and the fraction of surface that is covered by a given oxide [27]. Moreover, LEIS spectroscopy offers the capability to probe the very top layer of the growing oxide

3.2 Factors Affecting TGO Adherence

Although there is no universally accepted explanation for poor TGO scale adherence, there is a general understanding of the important factors that influence it. Adherence of the TGO scale is primarily affected by the following factors [8]:

(i) stresses in the scale which develop during scale growth and those associated with thermal cycling due to the difference in the thermal expansion between the substrate and the scale;

(ii) nucleation and growth of physical defects (*i.e.*, voids and microcracks) at the scale/coating interface and/or within the scale;

(iii) the growth rate of the TGO scale (*i.e.*, the tendency for scale spallation increases with increasing scale thickness);

(iv) solubity and interfacial segregation of certain elements, such as S and Ti, in both the metallic and ceramic components.

The composition and structure of the bond coat affect all of these factors. In relation to composition, Barrett [29] statistically analyzed the cyclic oxidation kinetics of 36 commercial aerospace alloys to arrive at phenomenological equations relating spallation behavior to alloy composition. Although these equations are not directly applicable to the bond coats in current TBC systems, they do effectively highlight the sensitivity of scale spallation to alloy composition and, in particular, the apparent interaction between alloying elements.

There is very little doubt that non-metallic impurities, particularly sulfur, in the bond coat or base alloy are very detrimental to scale adhesion [11,12]. Lee *et al.* [30] reported that with a low sulfur content in the aluminide coating (~0.1- 0.2 ppmw), the TGO scale was highly resistant to spallation at surfaces within the aluminide grains upon cyclic oxidation at 1150°C. Interestingly, however, the scale that formed over the grain boundaries of the coating spalled. This difference in scale adhesion behavior was attributed to the preferential segregation of heavy alloying elements, such as W, Ta and Re, from the substrate to the grain boundaries.

Whether a particular minor element is beneficial or detrimental to scale adhesion is often very dependent upon its content. For instance, Clemens *et al.* [31] showed that relatively high Ti contents (~2 wt.%) can be detrimental to Al_2O_3 adhesion on NiCrAlY-based coatings, whereas Al_2O_3 adhesion can be significantly improved if the NiCrAlY contains only 0.4 wt.% Ti. This dependence was ascribed to a change in the composition, structure and/or distribution of the different phases in the alloy matrix with increasing Ti content. Basically, the higher Ti content retarded formation of a homogeneous TGO scale due to subsurface stabilization of γ'-$Ni_3(Al,Ti)$ precipitates.

Reactive elements such as Y, La, Zr, Ce, and Hf at low concentrations of about 0.005-0.3 wt.% are also highly beneficial for improving scale adhesion, but are detrimental at concentrations greater than about 1 wt.% due to their tendency to form intermetallic phases that are prone to preferential oxidation [32].

It is now well established that the addition of platinum improves the oxidation behavior of β-NiAl based coatings [33-37]; however, the mechanisms of this beneficial effect are not well understood. Mechanisms that have been proposed include: enhanced aluminum diffusion in the β-NiAl (although no measurements have been made) thus allowing for the rapid re-formation of an Al_2O_3 scale following spallation [38]; mechanical keying or pegging of the Al_2O_3 scale to the Pt-modified coating [39]; stress relief of the Al_2O_3 scale [40]; exclusion of refractory metals from the outermost zone of the coating [41]; and increased stability of the β phase [37]. Other important factors may be the influence of platinum on the transformation of the Al_2O_3 from its metastable, faster-growing θ structure to its stable, more protective α structure, and the influence of platinum content and distribution on the establishment, growth and adherence of Al_2O_3 scale. These important factors have not yet been addressed in a systematic manner.

The beneficial effect of platinum on α-Al_2O_3 scale adherence is not limited to aluminide coatings. In fact, most studies on alumina-forming, platinum-containing alloys find that the presence of platinum improves α-Al_2O_3 scale adherence [20,42,43]. A limited number of studies have also indicated that the addition of a reactive element, such as yttrium or hafnium, further improves Al_2O_3 scale adherence on Pt-containing alloys. For instance, Allam *et al.* [42] found that Al_2O_3 scale adherence on alloys containing both platinum and hafnium was significantly better than on hafnium-free alloys in both isothermal and cyclic oxidation tests. Stott *et al.* [20] recently found that the addition of 2 wt.% Pt plus 0.2 wt.% Y significantly reduced the extent of Al_2O_3 scale spallation from directionally-solidified Ni-Al-Cr_3C_2 alloys under isothermal and cyclic oxidation at 1100 and 1200˚C in air. However, increasing the yttrium content to 0.7 wt.% had a detrimental effect on spallation resistance owing to the formation of Pt-Y intermetallics which consequently altered the homogeneity of the platinum distribution. It was inferred in the same study by Stott *et al.* that the incorporation of platinum into the alumina scale may have catalyzed the θ-Al_2O_3 → α-Al_2O_3 transformation, which is desirable from the standpoint of maximizing oxidation resistance. Pint *et al.* [7] recently reported that while the addition of platinum to NiAl is beneficial to alumina-scale adhesion, it is not as effective as hafnium or zirconium additions. These authors further reported that the addition of 0.05 at.% Hf to a β-NiAl(Pt) alloy had the effect of both improving alumina-scale adhesion and decreasing the α-Al_2O_3 growth rate by a factor of ten compared to the Hf-free alloy. It is likely that yttrium would have a similar beneficial effect; however, this has not been clearly established.

Moon and Lee [44] empirically quantified the tendency for a scale to spall during a temperature drop, ΔT, by the expression

$$\text{Tendency to spall} \propto \left[\frac{\zeta\,(\Delta T)^2}{\beta}\right]^m \qquad (1)$$

where ζ is the scale thickness before spalling, *m* is a positive number, which depends on the mechanical properties of the scale, and β is a constant which is dependent upon the strength of adhesion at the alloy/scale interface. The value of β increases with increasing strength of scale adhesion, while *m* typically varies from unity for a ductile scale to about 4 for a brittle scale. The values of β and *m* depend on the composition of the scale which, in turn, depend on the composition of the underlying alloy. In agreement with Eq. 1, Barrett and Lowell [45] concluded from their study of the cyclic oxidation behavior of commercial alloys at 1150˚C that the most critical factor in minimizing scale spallation is to keep the scale as thin as possible. Although not stated by Moon and Lee, it is clear from the recent results of Gleeson and Harper [46], who studied the long-term cyclic oxidation behavior of various commercial high-temperature alloys over the temperature range 982-1204˚C, that ζ, *m*, and β are actually cycle-dependent variables. Thus, accurate modeling of the cyclic oxidation behavior of alloys would require input variables which are time dependent (*i.e.*, cycle dependent). Such modeling has not yet been reported in the open literature.

3.3 Platinum-Modified Aluminide Coatings

As discussed above, platinum is a beneficial alloying addition for reducing Al_2O_3-scale spallation. The structural features and oxidation behavior of the various commercial platinum-aluminide coatings have been discussed by Patnaik *et al.* [34] and Streiff and Boone [36]. There is unanimous agreement that the varying structural features in these coatings are the cause for their wide variability in oxidation performance. Sometimes, however, conflicting results are reported. For instance, Sun *et al.* [47] reported the cyclic oxidation resistance of a platinum-aluminide coating at 1100°C is best if $PtAl_2$ is the principal phase at the coating surface. By contrast, Krishna *et al*. [48] reported that a coating outer layer consisting of NiAl + $PtAl_2$, with NiAl as the principal phase, provides the best cyclic oxidation resistance at 1100°C. *Clearly, the need exists to gain a better understanding of the effects of platinum content and distribution on the oxidation behavior of Pt-Ni-Al coating formulations.* Such an understanding will aid greatly in the advancement of platinum-aluminide coatings by providing target coating compositions and microstructures for optimum performance.

Full interpretation of the oxidation behavior of Pt-aluminide coatings (and alloys) is hindered by the fact that there is a paucity of information pertaining to the phase equilibria in the Ni-Al-Pt system. Such information is important not only from the standpoint of interpreting oxidation behavior, but also for the design of targeted, overlay coating compositions and constitutions. Figure 2 shows the only existing isotherm for the Ni-Al-Pt system published in the open literature [49]. The isotherm is actually based on the experimental observations by Jackson and Rairden [41] in their study of platinum-aluminide coatings on the Ni-base superalloy IN-738. The isotherm is for 1060˚C and is seen to be speculative. Moreover, there is evidence to suggest that the isotherm is incorrect. For instance, according to Mackie and Mart [50], who conducted X-ray diffraction analysis of Ni-Al-Pt alloys equilibrated at 1000˚C, there is no β-NiAl(Pt) + PtAl equilibrium, $PtAl_2$(Ni) exists over a wide composition range, and there is $PtAl_2$(Ni) + PtAl(Ni) equilibrium at higher platinum contents. In support of Mackie and Mart's findings, de Wit and van Manen [43] reported that a Ni-50 at.% Al-20 at.% Pt alloy was single-phase $PtAl_2$. These results are clearly at variance with the isotherm shown in Fig. 2. One of the first tasks of this project will be to accurately determine the phase equilibria in the Ni-Al-Pt system for which β-NiAl(Pt) is a constituent phase. Bulk alloys will be studied as opposed to coatings in order to negate the influence of diffusing substrate elements in the latter.

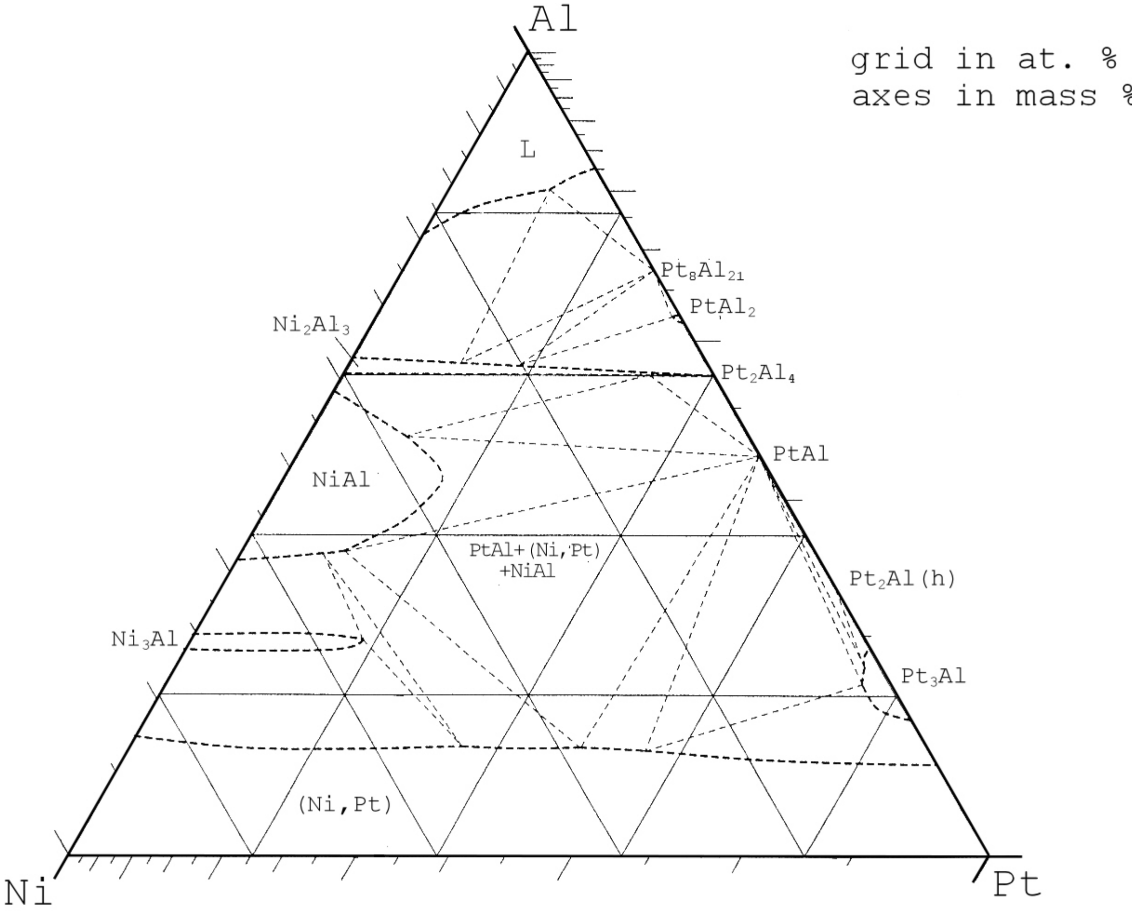


Figure 2 *Speculated 1060°C isotherm for the Ni-Al-Pt system [49].*

Optimization of microstructure and composition, together with reactive element (RE) additions, offer the strongest possibilities for increasing platinum-aluminide coating life. There is currently little or no systematic work reported in the literature which address these issues, particularly RE addition. The potential exists for platinum-aluminide coatings of tailored microstructures and compositions to be deposited via plasma spraying, which is a direct, physical deposition method. Plasma spraying provides a very useful tool for determining optimum overlay coating microstructures and compositions. Identifying an optimum microstructure would also aid in the design of similar coatings deposited by alternative overlay and non-overlay techniques.

3.4 Coating/Substrate Interdiffusion

As discussed earlier, bond coatings are also degraded by interdiffusion with the substrate. Since the bond coating is, by nature, higher in Al content than the substrate, Al diffuses from the coating into the substrate and generally becomes unavailable to support the growth of the protective alumina scale. Likewise, the Cr concentration in the MCrAlY overlay coatings is also typically greater than that in the substrate resulting in the diffusion of Cr from the coating into the substrate. In contrast, Ni and other elements (*e.g.*, Ti and Hf) in the substrate diffuse into the coating. Although the yttrium strongly affects adherence of the Al_2O_3 scale during cyclic oxidation, it is at such low concentration in the coating (*e.g.*, <0.2 at.%) that dilution by interdiffusion with the substrate is generally not considered. When a coating is substantially depleted of Al, it can no longer sustain exclusive Al_2O_3 scale growth. Less protective oxides, such as TiO_2 or $NiAl_2O_4$ can form signaling the end of the protective life of the TBC system. A critical element content in the coating at the coating/TGO interface (*e.g.*, Al or Ti) can be defined to indicate the useful life of the coating. This critical content could indicate the time at which less-protective oxides form on the surface. Modeling the element transport in the coating and substrate during oxidation allows the coating life to be predicted. The purpose of this aspect of the present work will be to further develop a one-dimensional ternary diffusion model to predict the concentration profiles associated with the oxidation and interdiffusion of coated superalloys during service. The original model was developed by Dr. James Nesbitt (a collaborator in the proposed project) at the NASA Glenn Research Center and was given the name COSIM for Coating Oxidation and Substrate Interdiffusion Model. The model employs finite-difference techniques embodied in a FORTRAN computer program to provide numerical solutions to the appropriate diffusion equations. The computer code employs numerous subroutines to make the program flexible and modifiable to more complex coating systems, so that, for example, diffusion of various elements from the substrate may be considered. In addition to COSIM, the commercially available software package *DICTRA* (standing for Diffusion Controlled TRAnsformations) will be used. *DICTRA* offers the advantage of simulating diffusion in multicomponent, multiphase systems; however, its application to bond coat/substrate systems is not yet possible due to lack of an appropriately complete database. Initial effort in the coating/substrate interdiffusion aspect of the proposed research program will be to determine (approximately) the phase equilibria and interdiffusion data required by *DICTRA*.

The dependence of coating/substrate interdiffusion behavior on Pt-modified aluminide coating composition has not yet been systematically investigated. An understanding of such a dependence is important in the determination of the critical factors affecting Pt-modified aluminide coating performance. Accordingly, the COSIM and *DICTRA* programs will be extensively applied to the Pt-modified aluminide coatings to be studied in this program.

An additional important concern during the interdiffusion between a coating and a nickel-base superalloy is the formation of topologically close-packed (TCP) phases, such as sigma (σ), mu (μ), and R. The morphology of TCP-phase precipitates is typically plate-like or needle-like, and formation of even a few volume percent TCP phase is considered to be deleterious to the strength and toughness of the coating/alloy system. TCP-phase formation is promoted by deformation and, perhaps more importantly, the presence of refractory metal elements Re, Mo, W, Cr, and Ta [51]. Thus, with the introduction of significantly higher levels of rhenium in the current third generation superalloys for the purpose of improving creep-rupture strength, TCP-phase formation resulting from coating/substrate interdiffusion is becoming an increasingly important issue

The benefits gained from the interdiffusion component of the proposed study are of both fundamental and practical significance. The fundamental significance lies in an increased understanding of the effects of composition on coating/substrate interdiffusion which, in turn, aids in the design of coating/substrate systems having increased prime reliance. The practical significance lies in the increased ability to design robust coatings and to predict coating service life.

3.5 Life Prediction of TBC Systems

There is general agreement that the occurrence of TBC spallation requires both thermal cycling and oxidation [5,6]. Both of these factors have been linked in a general understanding that could be termed "mechanical effects", where the chemical effect of oxidation is a contributor to the mechanical effect of subcritical crack growth during thermal cycling [52]. While mechanical effects can be viewed as a unifying view to understanding spallation, it is clear from virtually all work that oxidation, and the effects related to oxidation, are the principal factors dictating TBC spallation. This is especially true for PVD coatings where it is commonly observed that coating life is relatively independent of the number of thermal cycles, but is closely tied to the total time the coating is at high temperature. As mentioned in the Introduction of this proposal, several investigators have taken this point further to assert that TBC spallation is related to a "critical TGO scale thickness". Such life prediction of spallation is primarily prediction of a rate to reach an end point, and since oxidation is rate controlling, life-prediction models based on oxidation have been very successful [5,6,53,54]. In fact, all models that are currently in use for predicting TBC life in production systems are in essence oxidation based. The downside of these models is that they all use empirical descriptions of both oxidation and the relationship between extent of oxidation and spallation.

Numerous studies in the oxidation and TBC literature have shown that oxide and TBC spallation can vary dramatically with the base metal under identical bond coats as well as varying dramatically with variations in bond coat composition and structure [8]. While early explanations of this phenomenon attributed differences in spallation life to differences in CTE and mechanical properties of the various base metals, more recent data have shown that minor additions to the base metal, such as yttrium or titanium, can cause anywhere from a factor of 2 to 5 change in TBC lifetime with no change in base metal mechanical properties [55]. While mechanical models may be able to describe <u>why</u> this occurs, chemical-based models are required to predict <u>when</u> this will occur.

Oxidation-based models have been shown to work well for a wide variety of TBC systems, albeit with varying constants in the Arrhenius description [5]. The reason these models work well is that all oxidation effects on TBC spallation can be related to diffusion-related phenomena, such as: TGO growth rate, including variations in rates of transient oxidation; differing rates of diffusion in differing bond coat and base metal compositions and structures; breakdown of certain "diffusion barrier" phases with time and temperature; and variations in interfacial effects, such as surface segregation of impurities (*e.g.*, sulfur). However, in order for these oxidation-based models to be predictive outside the experience base, these diffusion mechanisms must be addressed from a fundamental point of view. An interesting example from unpublished Rolls-Royce Allison data [B. Brindley, personal communication] illustrates the merit of an approach that addresses diffusion-related issues. TBCs on base-metal coupons containing titanium were found to have a shorter life than those on base metals with identical compositions and bond coats, but very low levels of titanium. Both systems showed similar scaling behavior over short times when β-NiAl(Pt) was the continuous phase at the bond coat surface. At longer times, when the β-phase, which has an inherently low solubility for titanium, started to transform to γ′-Ni_3Al, which has a higher solubility for titanium, there was a tendency for the TBC on the Ti-containing base alloy to spall, while the TBC on the low-Ti alloy maintained adherence. The coating life in this case appeared to be related to both diffusion processes that lead to β→ γ′ transformation and diffusion of titanium to the TGO/bond coat interface. Thus, the mechanical effect, an expected drop in interfacial toughness of the scale, is tied to the rate of phase transformation and to the rates of diffusion through the phases. The results highlight the importance of the coating/substrate interdiffusion component of the proposed study (see Section 3.4 for more detail).

A useful mechanical parameter for assessing the quality of the bond coat/TGO interface is the adhesion energy per unit area (interface fracture toughness, J/m^2), designated Γ_i. *A major advancement in the life prediction modeling of TBC systems could be made if the interfacial toughens and adhesion are systematically studied in terms of the chemistry and microstructure of the bond coat /TGO interface.*

4. Plan of Research Program

The methodology of the proposed research program has been designed to address the objectives stated in Section 2. The program is highly integrated, with the results often being complimented and/or used in different objectives.

4.1 Objective 1: *Determine the chemical and structural factors governing exclusive formation of a thin, non-porous and adherent α-Al_2O_3 scale.*

The alloy systems to be studied under this objective will be based on Ni-Co-Cr-Al-Y and Ni-Al-Pt formulations. The specific chemical and structural factors that will be studied are:

composition:
- alloy phase constitution (β, $\beta+\gamma$, $\beta+\gamma'$, $\gamma+\gamma'$) and phase composition
- addition of minor amounts (0.5-3 wt.%) of metallic elements (*e.g.*, Ti, Hf, Y, and Re) to the alloys
- presence of indigenous non-metallic elements (*e.g.*, S and C) in the alloys

structure:
- distribution of the different phases within the alloys
- volume fraction of different phases within the alloys
- single crystalline versus polycrystalline

surface condition:
- nature and composition of the native passive oxide layer present at room temperature
- pre-oxidization at a high temperature under controlled conditions in which the oxygen partial pressures, P_{O_2}, range from *ca.* 10^{-6}-10^{-25} atm.

All of these interrelated factors can have an effect on the alloys' ability to form a thin, non-porous and adherent α-Al_2O_3 scale. The majority of the alloys to be studied are multiphase and, as such, have a limited fundamental foundation from which to predict or assess their oxidation behavior. As recently reviewed by Gesmundo and Gleeson [56], theoretical treatments of multiphase alloy oxidation are very limited and, at best, semi-quantitative. Indeed, from a thermodynamic point of view, there should be no distinction between the oxidation behavior of single-phase and multiphase materials. This is because under equilibrium conditions the chemical activity of any given component is the same in all phases, regardless of how large the concentration difference may be. However, it is component concentration and general availability, not activity, that dictates oxidation behavior (*i.e.*, kinetic factors predominate over thermodynamic).

Tests will involve commercial MCrAlY and NiAl-Pt bond coats (supplied by Rolls-Allison Engine Company through its vendors), bulk alloys having the phase constitutions β, $\beta+\gamma$, $\beta+\gamma'$, and $\gamma+\gamma'$, and novel vacuum plasma sprayed (VPS) coatings based on selected bulk alloy compositions. The VPS coatings will be deposited in-house using the plasma-spray facilities managed by Prof. [redacted] (co-Principal Investigator). The substrate material for all coatings will initially be the single-crystal, nickel-base superalloy CMSX-4 (supplied by Cannon-Muskegon). Subsequent years will utilize modified CMSX-4 alloys containing additions of reactive or other elements known or found to be either beneficial or detrimental to TGO adherence and mechanical integrity. The aim with the modified alloys is to ascertain how the potential influence of a given substrate element is affected by bond coat structure and composition. In a similar manner, the bulk alloys will be modified with minor additions (0.5-3 wt.%) of Ti, Hf, Y and Re in order determine if a critical content exists for each of these elements and for a given phase constitution, beyond which TGO adherence and mechanical integrity deteriorates. The effects of sulfur and carbon will be monitored initially by determining their indigenous contents in the alloys; a number of subsequent tests will investigate the effects of sulfur and carbon removal (via a hydrogen annealing process developed by James Smialek at NASA Lewis). In addition, NiAl-based single crystals will be studied (as discussed below). All alloys will be assessed using the thermodynamic software package *Thermo-Calc*.

In order to meet Objective 1, studies have been divided into two primary tasks: (1) Passive/Transient Oxide Characterization and (2) Long-Term Isothermal and Cyclic Oxidation. Task 1 (discussed in more detail below) involves detailed and fundamental investigations of passive oxide formation as a function of alloy composition, alloy structure, and oxidation conditions. Included in this task is the characterization of the room-temperature passive oxide layers on the various alloys. In addition, transient evolution of the initial oxide in terms of oxide morphology and phase changes, incorporation of diffusing species and defect formation as the oxide thickness increases will be investigated within this task. Task 2 (also discussed in more detail below) will focus on scale formation during long-term isothermal and cyclic oxidation as a function of alloy composition and structure. In addition, the effect of pre-oxidation will be examined. For the first 2-3 years of Task 2, all samples will be tested without a YSZ topcoat, while in years 3-5 selected samples will be tested with a YSZ topcoat. For all long-term tests, the quality of the TGO scale will be assessed based its adherence, thickness, homogeneity, and structure. Comparative quantification of the scale qualities will be provided by mechanical-property measurements, as outlined in Objective 4. Analyses of the Task 2 results will draw on knowledge gained in Task 1.

The topcoats to be deposited on selected bond-coat compositions, as determined in the first 2-3 years of this Objective, will be EB-PVD YSZ. The topcoats will be deposited by a vendor for Rolls-Royce Allison. The bond-coat compositions will cover a range of oxidation behaviors, thus allowing for a systematic investigation of the performance of TBC systems. The topcoated samples will be tested via cyclic oxidation in air at 950-1200°C for at least 1000 h. Coating failure criterion will be loss of *ca.* 20% of the coating.

Bulk Alloy Preparation and Characterization: Buttons (~100 g) of the various bulk alloys to be studied will be prepared by argon arc-melting. Approximately six compositions of a given phase constitution will be prepared initially (giving a total of 24 alloys). The initial alloys will not contain intentional minor additions, as these will be studied in subsequent years. Where applicable, nominal compositions of current commercial bond coatings will be prepared. For example, a typical $\beta+\gamma$-NiCoCrAlY coating contains (in wt.%) *ca.* Ni-15Co-18Cr-10Al-0.5Y, while a β-NiAl-Pt coating contains *ca.* Ni-35Al-10Pt. The as-cast buttons will be equilibrated in argon at 950, 1050, and 1200°C, characterized using standard metallographic techniques, and then phase analyzed using X-ray diffraction (XRD), electron probe microanalysis (EPMA), and wet chemical analysis (the latter will be done in order to determine the overall alloy composition). Equilibration will be verified by annealing selected alloys for different times at a given temperature and noting if the phase compositions are dependent (non-equilibrated) or independent (equilibrated) of time. The initial annealing period will be for one week. The results from the characterizations (*i.e.*, phase compositions and volume fractions) will be compared with those predicted using *Thermo-Calc*. A powerful feature of the *Thermo-Calc* system is that it contains a subroutine for thermodynamic assessment, in which experimental data can be taken into account to develop and/or extend the databases.

Single crystals will be used for some of the studies described for Task 1. These will either be purchased or prepared in-house by common single crystal growth techniques. One particular advantage of the in-house facilities is that crystals with "impurities" (such as C, S, Ti, Hf, Y, and Re) can be custom prepared in a timely fashion.

Deposition of Vacuum Plasma Sprayed Coatings: Powders for the plasma-spray coating process will be procured from commercial venders or, if necessary, produced in-house by the gas atomization process. The substrate will be approximately one-inch diameter discs of CMSX-4.

The plasma-spray process is well-suited for depositing coatings with targeted compositions. The coating process will be carried out within a 100 ft^3 chamber under an inert (*e.g.*, argon) atmosphere. Moreover, the pressure of the inert environment can be controlled from ambient down to nominally 50 torr. This adds greater flexibility in changing the as-deposited microstructural features (*e.g.*, porosity and grain size and shape) of the coating and reduces the amount of oxygen incorporation into the coating.

The as-deposited coatings will be analyzed using XRD, EPMA, scanning electron microscopy (SEM), and optical microscopy (OM).

Task 1 – Passive/Transient Oxide Characterization

The purpose of this task is to address the following questions:

1. To what extent is the structure, thickness, and composition of the native passive oxide that forms on the various alloy surfaces controlled by the alloy composition/structure?
2. Can metastable, deleterious oxide phases be avoided during the transient stage by controlling oxidation conditions?
3. Does the presence of particular elements (e.g., Pt, Y, Hf, C, S) alter oxide development in either the passive or transient stage of oxide growth?
4. How does the structure and composition of the passive oxide affect transient oxide growth?

To address these questions, systematic studies are necessary. The room-temperature, native passive oxides of the various alloys and coatings described above will be examined. These oxides will be characterized both chemically and structurally using XPS and LEIS, together with high-resolution scanning Auger microscopy (SAM) and SEM. XPS will be used to access the passive oxide thickness. Once the room-temperature, native passive oxides have been examined, the effects of oxidation environment on passive oxide characteristics will be studied. To do this, select samples, including the single crystals, will be cleaned to < 5 % of a monolayer of contaminants via either fracturing or sputtering followed by annealing under ultrahigh vacuum

(UHV) conditions (< 5 x 10^{-10} Torr). A passive oxide will then be produced within the UHV chamber using either dry or moist oxygen. Further studies will involve producing a clean surface in vacuum, removing these surfaces from the UHV chamber and introducing them into an atmospheric pressure environment with a controlled humidity. The passive oxide layers formed would then be studied in the same fashion as the native oxides and compared. In all cases, the passive oxide layer formed is expected to be no more than about 125 Å thick

The single crystals used above will contain a limited number of elements (*e.g.*, Ni-Al-Pt and Ni-Al-Y). The use of single crystals will allow structural characterization of the oxides that might otherwise be unfeasible with multicomponent commercial alloys. Moreover, the comparison of oxide growth on polycrystalline versus single crystalline samples can be conducted to determine the effect of alloy structure on oxide development. Furthermore, detailed effects of the addition of minor constituents can be examined. The room-temperature, native passive oxides on these samples will help access phase-specific oxide characteristics. Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) will be used as appropriate to augment these studies.

Of particular interest are the influences of the passive oxide layer on (i) the subsequent transient stage of oxide development and (ii) the ultimate final structure of the TGO. This may be considered to be a rather fundamental query, but this specific aspect of oxidation, particularly with the complex alloys used in substrate and bond coat alloys, has not been thoroughly studied. As discussed earlier, environmental conditions significantly affects oxide development during the transient stage; therefore, it is quite reasonable to expect an influence of the initial oxide formation on the transient stage of oxide growth.

The transient stage of oxidation will be studied both within the ultrahigh vacuum chamber and under atmospheric conditions. Within the UHV chamber, both clean samples and samples produced *ex situ* with native passive oxides will be exposed to oxygen and oxygen-steam environments at temperatures ranging from 25-1000°C. Oxides in the transient stage are expected to be less than 1 μm in thickness. Transient oxides will be studied not only by XPS, LEIS and SEM/SAM but also by TEM and X-ray diffraction. The thicker oxide layers will be examined by *in situ* fracturing within the SEM/SAM apparatus. This portion of the task will be specifically assessing what materials and under what conditions stable α-Al_2O_3 scale growth is favored.

This task will involve the training of 1 PhD and 2 MS students over the five years of the program, plus 1 undergraduate student for each of the five years.

Task 2 – Long-term Isothermal and Cyclic

Similar to Task 1, the commercial bond coats, bulk alloys, and lab-scale VPS coatings will be studied in coupon or disc form. As stated earlier, samples will be tested without a YSZ topcoat during the first 2-3 years of the task, while in years 3-5 selected samples will be tested with a YSZ topcoat. All samples will be exposed to air under isothermal and temperature-cycling conditions at 950, 1050, and 1200˚C for up to 3000 h. the bond coats will be tested in both pre-oxidized and “bare” conditions. Pre-oxidation will involve isothermally oxidizing the samples under controlled atmospheres having an oxygen potential of *ca.* 10^{-6}-10^{-25} atm, thus facilitating the development of a continuous, high-purity α-Al_2O_3 scale prior to long-term oxidation testing in air.

Temperature cycling will consist of repeated one hour exposures at temperature followed by cooling to room temperature and then raising to the oxidation temperature again. The coupons will be tested in batches, thus allowing for high throughput and repetition of testing. The tests will be continued up to 3000 h or until significant spallation of the scale occurs; however, coupons will be removed for full examination after various periods of exposure to ascertain the progress from the early stages of scale growth to, perhaps, eventual failure.

Relationships between alloy and bond coat structures and compositions, temperature, cycling regime and scale adherence/spallation will be established. Isothermal and cyclic oxidation kinetics will be determined on the basis of both weight change and scale + affected subsurface zone thickness. The oxidized coupons will be examined metallographically and the scale/subsurface regions compositionally and structurally characterized. The methods of analysis will include XRD, EPMA, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and optical microscopy (OM). Particular emphasis will be placed on determining element concentrations in the bond coat, in the scale, and at the interface as a function of oxidation time.

The essential questions to be addressed include:

1. What are the oxidation kinetics and how do they correlate with specific element content and distribution in the alloy/coating?
2. What is the morphology, phase constitution and composition of the TGO scale both as function of time and alloy/coating composition?
3. What changes occur in the subsurface of the alloys/coatings as a consequence of the oxidation process? Do these changes have an effect on oxidation behavior and TGO properties?
4. What is the effect of oxidizing temperature on overall oxidation behavior?

By addressing these questions, a more detailed understanding will be gained of the effects of microstructure and composition on α-Al_2O_3 scale formation and quality.

This task requires an extensive amount of testing and analyses. Accordingly, the task will involve the training of 5 PhD and 3 MS students over the five years of the program, plus 3 undergraduate students for each of the five years. The task will also involve the training of a postdoctorate researcher.

4.2 Objective 2: *Determine optimum platinum-modified aluminide plasma-sprayed coating compositions and structures for improved high-temperature oxidation resistance.*

This objective overlaps with the NiAl-Pt component of Objective 1. The results from β-NiAl-Pt analyses in Objective 1 will be used for partial determination of the Ni-Al-Pt isotherms. Of particular interest are the solubility limits for platinum in β-NiAl as a function of β stoichiometry and the various phase equilibria associated with β. In this Objective, additional Ni-Al-Pt alloys (~5 g buttons) will be fabricated, equilibrated, and then chemically analyzed in order to more completely determine the various phase equilibria associated with β. The effects of 0.5-3 wt.% Y, Hf, Ti, and Re additions on the phase equilibria in the Ni-Al-Pt will also be determined (*i.e.*, the systems will be treated as quasi ternary). The information gained from this portion of Objective 2 will be utilized both in the determination of target coating compositions and in the interpretation of the oxidation and coating/substrate interdiffusion behaviors.

Based on the first-year results from Objective 1, a range of VPS coating compositions will be deposited onto a CMSX-4 substrate. Target compositions will be achieved by mixing powders of $PtAl_x$ and Ni_xAl_y. Various Ni_xAl_y powders are available from commercial venders, whereas the $PtAl_2$ powders have already been produced in-house by the gas atomization process and are available for the proposed program through an ongoing collaboration at ISU between [redacted] Additional $PtAl_x$ powders can be processed if necessary. Coatings will be deposited as described for objective 1. Coatings with reactive element (RE) additions of yttrium and/or hafnium will be deposited by alloying these elements into the starting $PtAl_x$ powders during gas atomization.

Coatings will be prepared by first mixing the $PtAl_x$ and Ni_xAl_y powders according to the mass ratios required. This will lead to a uniform mixture of discrete $PtAl_x$ and Ni_xAl_y phases distributed throughout the coating (see for example Fig. 3 from the collaborative study being conducted by [redacted] The as-deposited coating microstructures may be further tailored by separately feeding $PtAl_x$ and Ni_xAl_y powders into the plasma gun. By controlling the mass feed rate of each powder, it is quite simple to form a coating with predetermined variations of phase contents throughout the thickness of the coating. For instance, the fraction of $PtAl_x$ within a Ni_xAl_y matrix can be varied from 0 vol.% at the substrate interface to 100 vol.% at the coating surface. This variation can be in discrete levels or can be made to approximate a continuous gradation.

The as-deposited coatings of different compositions, phase constitution and phase distribution will be analyzed using XRD, EPMA, SEM, and OM. Coupon samples of the as-deposited coatings will also be vacuumed annealed at 950-1200°C for both one and two weeks in order to allow equilibration and also to gain insight into the extents of coating/substrate interdiffusion (Objective 3).

As-deposited, coated alloy coupons without a topcoat will be exposed to air under isothermal and temperature-cycling conditions at 950, 1050, and 1200˚C for up to 3000 h. Coupons with a currently used, platinum-aluminide diffusion coating will also be tested in order to provide baseline data. Subsequent tests will involve topcoats. The procedures and methods of analyses

***Figure 3** SEM micrograph of plasma-sprayed ß-NiAl + $PtAl_2$ coating. Dark and light phases correspond to NiAl and $PtAl_2$, respectively.*

will be the same as discussed for Objective 1. Of specific interest are the effects the effects of coating composition and microstructure on the ability to form an adherent and slow-growing α-Al_2O_3 scale. Similar to Task 2 in Objective 1, oxidation tests will involve exposure of both pre-oxidized and “bare” samples to air under both isothermal and temperature-cycling conditions at 950-1200°C.

A significant benefit of the work proposed in this objective is that plasma-spray deposits are usually quite close to the composition of the starting material. Consequently, there is no need for an extensive, costly development portion of the current program to fabricate the correct RE additions to the coating compositions. This allows the currently proposed program to quickly establish the merit of RE additions to platinum-aluminide coatings. Moreover, the plasma spraying of platinum-aluminides provides an effective way to inexpensively determine whether extensive development of alternate overlay-type processes (*e.g.*, EB-PVD) is worthwhile.

This objective will involve the training of 1 PhD and 3 MS students over the five years of the program, plus 1 undergraduate student for each of the five years. This effort will also involve the training of a postdoctorate researcher.

4.3 <u>Objective 3</u>: *Determine the effects of bond coat and substrate compositions on the kinetics and behavior of coating/substrate interdiffusion.*

Tested coated samples from objectives 1 and 2 will be extensively analyzed to determine the effects of time, temperature, and coating and substrate compositions on the extents of interdiffusion. Additional coated samples and bulk alloy/CMSX-4 diffusion couples will be heated for 50-1000+ hours at 950, 1050, and 1200°C. The times will be such so as to allow for a full characterization of the interdiffusion processes.

The microstructural and compositional changes which occur in the various systems will be analyzed using EPMA, SEM, OM, and, if necessary, TEM. The electron microprobe is ideally suited for measuring interdiffusion and obtaining detailed chemical information.

From the various analyses, the essential questions to be addressed are:

1. The stability of the coating structure as a function of both time and temperature.
2. The rates of interdiffusion vary with coating and substrate compositions and how do these rates correlate with coating oxidation behavior.
3. The existence critical concentrations due to diffusive enrichments or depletions that can be used to monitor coating life.
4. The principal diffusing species. (Determine with the aid of the diffusion path concept.)
5. The initial rates of interdiffusion as compared with the interdiffusion rates at later stages of coating life.
6. The reaction zone constitutions and morphologies and how do they vary with time, temperature, and coating and alloy compositions. (Of specific interest is TCP-phase formation.)

By addressing these questions and applying the results to both the COSIM and *DICTRA* (see section 3.3), it will be possible to estimate the useful lifetime of a given bond coating of a particular composition and thickness.

The EPMA results will also be entered into a regression model developed by Ritzert *et al.* [51] which predicts TCP content as a function of composition. Comparison will be made between actual and predicted TCP contents, and modifications made to the regression model if necessary.

This objective will involve the training of 1 PhD and 2 MS students over the five years of the program, plus 1 undergraduate student for each of the five years.

4.4 Objective 4: *Determine relative composition- and time-dependent mechanical parameters associated with the TGO*

The integrity of the TGO scales formed on different systems will be assessed and correlated with the chemistry and structure of the substrate based on several gauging parameters. The oxide integrity will be assessed based on its physical and mechanical characteristics as well as the level of residual stresses and the corresponding microstructure changes of the substrate. The topography of the oxide and its structure will be analyzed to characterize any surface wrinkling and defect formation. The interfacial fracture toughness of the oxide layer will be evaluated by destructive mechanical testing. The fracture toughness of the TGO layer will be tested for a representative grouping of alloys and coatings.

Interfacial Fracture Toughness: Several standard methods are used to evaluate the interfacial fracture toughness for coating systems [57]. In the proposed work, two complementary techniques will be utilized. In the First, a wedge impression will be used on the oxide/substrate system, after removing a slice of the oxide equivalent to the indenter width for limiting the initial damage. The interfacial fracture toughness is evaluated from [58]

$$\Gamma_i = \Gamma_i(a, E_t, E_g, h_t, h_g, \varepsilon_{rg}, \varepsilon_{rt}, \varepsilon_i) \qquad (2)$$

where a is the extent of the delamination front, ε_i is the substrate strain at the delamination front (evaluated through FEM calibration), and ε_{rg} and ε_{rt} are the residual strains in the grown oxide and the TBC topcoat respectively. In the second, a rectangular specimen with the oxide or oxide and topcoat will be uniformly compressed in order to address the spatial distribution of spalling. If the delamination process is unstable, a grooved coating will be used to arrest the delamination front. The interfacial fracture toughness has a phenomenological expression similar to Eq. (2).

The adhesion of the oxide layer to the different TCP phases within the substrate will be addressed qualitatively by using the nanoindenter at Oak Ridge National lab, a collaborator on this proposal. The indenter will be driven to a depth larger than the oxide thickness and the extent of debonding measured. With significant statistics, these measurements will provide the spatial dependence of the interfacial fracture toughness on both the history of thermal cycling and the substrate composition and homogeneity. Such data, which are essential for life prediction modeling, do not exist.

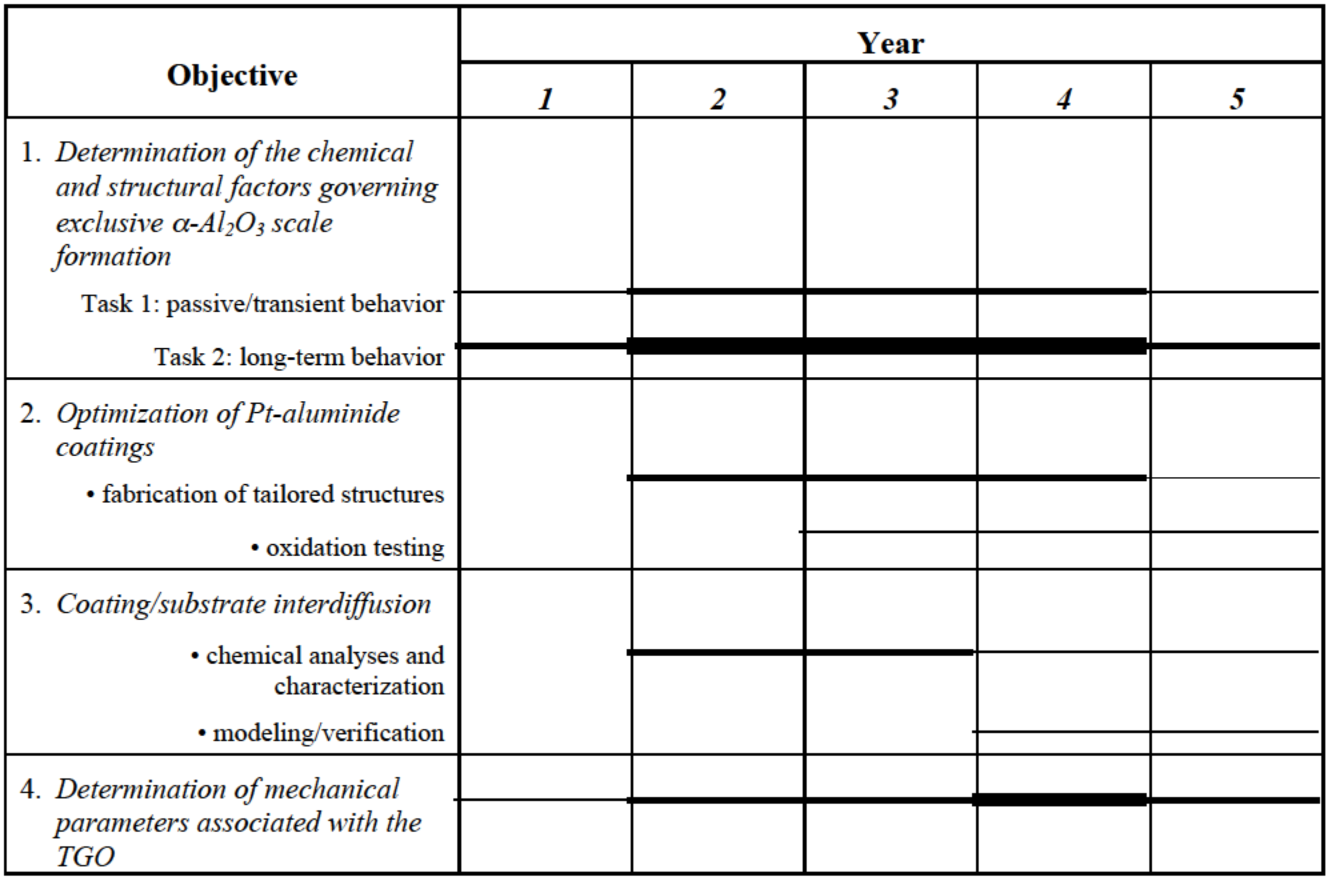
Residual Stresses: For a thin film on a brittle substrate, residual stresses can be accurately measured by laser curvature measurements [59]. However, for a ductile substrate, creep relaxation, especially at higher temperatures, renders this technique invalid. Instead, stresses are best assessed using micro-Raman spectroscopy (MRS) [60], wherein residual stresses induce frequency shift in a laser beam, focused on the surface. Such a system has a micron level spatial resolution. Initially, the MRS system at Oak Ridge National Laboratory, which is a collaborator in our program, will be used. Concurrently, a similar system will be built at ISU. The ISU system will be attached to an oxidation chamber. The MRS measurements will provide the stress-thermal cycling oxidation history. When a full TBC system (*i.e.*, with topcoat) is tested, the thermal mismatch stresses will be calibrated first and then deconvoluted to yield the growth stresses.

A second technique will be used to qualitatively resolve the spatial distribution of stresses with the needed resolution. It is based on monitoring the evolution of the deformation field through digital image correlation, whereby pairs of digital images are captured (either optically using a telescopic lens or via Infrared) during the loading history and compared via Fourier transform or a correlation function to find the relative displacement vector field [61].

This objective will involve the training of 1 PhD and 3 MS students over the five years of the program, plus 1 undergraduate student for each of the five years.

5. Timings

The chart below presents an estimate of the timings for the four objectives of the proposed project. The project would be for 5 years, commencing April 30, 2000 and finishing April 29, 2005. The thicknesses of the timelines in this chart correspond to level of output as determined by graduate student involvement (see Section 6).



6. Research Training of Students in Science and Engineering

The proposed program relies heavily on support and contributions from both graduate and undergraduate students. The students will be given hands-on experimental opportunities, exposure to practical experience through close interactions with the Principal Investigators and theoretical training in their complementary coursework. Moreover, the synergy of the assembled program will offer a unique advantage for the students to move beyond their respective disciplines and gain detailed exposure to different, yet closely related technical areas.

The Principal Investigators will each supervise a number of M.S. and Ph.D. students throughout this program. As is the common practice at Iowa State University, undergraduate students will participate as key members of this work to gain practical experience and hopefully develop a desire for post-graduate studies. Two post-doctoral fellows will be employed to help direct the isothermal and cyclic oxidation studies and the development of the Pt-modified Ni-Al coating systems. The collective number of graduate (M.S. and Ph.D.), undergraduate (UG) students and post-doctoral fellows proposed for each year of this program is shown below together with the cumulative total of each participant for the entire program:

Year 1	Year 2	Year 3	Year 4	Year 5	Cumulative Total
4 Ph.D.	9 Ph.D.	9 Ph.D.	9 Ph.D.	4 Ph.D.	9 Ph.D.
0 M.S.	4 M.S.	5 M.S.	6 M.S.	5 M.S.	10 M.S.
7 UG	7 UG	7 UG	7 UG	7 UG	7 UG
2 PDF	2 PDF	2 PDF	2 PDF	2 PDF	2 PDF

7. References Cited

1. National Research Council, *Coatings for High-Temperature Structural Materials: Trends and Opportunities*, National Academy Press, Washington, D.C., (1996) p.5.
2. S.M. Meier and D.K. Gupta, "The Evolution of Thermal Barrier Coatings in Gas Turbine Engine Applications", *Trans. ASME*, **116** (1994) 250.
3. E.A.G. Shillington and D.R. Clarke, "Spalling Failure of a Thermal Barrier Coating Associated with Aluminum Depletion in the Bond Coat", *Acta Mater.*, **47** (1999) 1297.
4. B. Barber, E. Jordon, M. Gell, and A. Geary, "Assessment of Damage Accumulation in Thermal Barrier Coatings Using a Fluorescent Dye Infiltration Technique', *J. Therm. Spray Technol*., **8** (1999) 79.
5. S.M. Meier, D.M. Nissley, and K.D. Sheffler, "Thermal Barrier Coating Life Prediction Model Development", NASA Contractor Report 189111 (1991).
6. R.A. Miller, "Oxidation Based Model for Thermal Barrier Coating Life", *J. Amer. Cer., Soc*., **67** (1984) 517.
7. B.A. Pint, I.G. Wright, W.Y. Lee, Y. Zhang, K. Prüßner, K.B. Alexander, "Substrate and Bond Coat Compositions: Factors Affecting Alumina Scale Adhesion", *Mater. Sci. Engin*., **A245** (1998) 201.
8. W.J. Quadakkers, A.K. Tyagi, D. Clemens, R. Anton, L. Singheiser, "The Significance of Bond Coat Oxidation for The Life of TBC Coatings", in *Elevated Temperature Coatings: Science and Technology III*, J.M. Hampikian and N.B. Dahotre (Eds.), TMS, Warrendale, PA (1999) p.119.
9. E.C. Dickey, B.A. Pint, K.B. Alexander, I.G. Wright, "The Effect of Platinum on the Growth and Adhesion of α-Al_2O_3 Scales", in *High Temperature Surface Engineering*, J. Nicholls (Ed), in press.
10. E. Basuki, A. Crosky, and B. Gleeson, "Interdiffusion Behavior in Aluminide-Coated Rene 80H at 1150°C, *Mater. Sci. Engin. A*, **A224** (1997) 27.
11. R. Prescott and M.J. Graham, "The Formation of Alumina Oxide Scales on High-Temperature Alloys", *Oxid.*

Met., **38** (1992) 233.

12. F.H. Stott, “The Oxidation of Alumina-Forming Alloys”, *Mater. Sci. Forum*, **251-254** (1997) 19.
13. J. Jedlinski and G. Borchardt, “On the Mechanism of Alumina Formers”, *Oxid. Met.*, **36** (1991) 317.
14. D.M. Lipkin, D.R. Clarke, M. Hollatz, M. Bobeth, W. Pompe, “Stress Development in Alumina Scales Formed Upon Oxidation of (111) NiAl Single Crystals”, *Corros. Sci.*, **39** (1997) 231.
15. J. Doychak, “Oxidation Behavior of High-Temperature Intermetallics”, in *Intermetallic Compounds, Chapter 43, Vol. 1*, J.H. Westbrook and R.L. Fleischer (Eds), New York, Wiley & Sons (1994) pp. 977-1016.
16. W. Lih, E. Chang, B.C. Wu, and C.H. Chao, “Effects of Bond Coat Preoxidation on the Properties of ZrO_2-8wt.% Y_2O_3/Ni-22Cr-10Al-1Y Thermal-Barrier Coatings”, *Oxid. Met.*, **36** (1991) 221.
17. J.C. Schaeffer, “The Effect of Alumina Phase Transformations on Thermal Barrier Coating Durability”, in proceeding to *TBC Workshop 1997*, NASA Lewis Research Center, Cleveland, OH, (1997) pp.99-108.
18. W.C. Hagel, “The Oxidation of Iron-, Nickel-, and Cobalt-Base Alloys Containing Aluminum”, *Corros.*, **21** (1965) 316.
19. B.A. Pint, “The Oxidation Behavior of Oxide-Dispersed β-NiAl: I. Short-Term Performance at 1200°C”, *Oxid. Met.*, **49** (1998) 531.
20. F.H. Stott, B. Gleeson, P. Castello, “The Effect of Platinum Additions on the Oxidation of Directionally-Solidified Ni-Al-Y-Cr_3C_2 Alloys at 1000 and 1200˚C”, *Mater. High Temp.*, (1999).
21. I. Kvernes, M. Oliveira, P. Kofstad, “High Temperature Oxidation of Fe-13Cr-XAl Alloys in Air/H_2O Vapor Mixtures”, *Corr. Sci.*, **17** (1977) 237.
22. R. Ramkumar, G.H. Meier, and F.S. Pettit, “The Effect of Water Vapor on the Oxidation of Alloys that Develop Alumina Scales for Protection”, to be published (1999)
23. J.L. Smialek, C.A. Barrett, and J.C. Schaeffer, “Design for Oxidation Resistance”, *ASM Handbook, Vol. 20: Materials Selection and Design*, ASM International, Materials Park, OH, (1997) p. 589.
24. B. Ahmad and P. Fox, “STEM Analysis of the Transient Oxidation of a Ni-20Cr Alloy at High Temperature, *Oxid. Met.*, **52** (1999) 113.
25. J. Goldstein, S. Choi, F.J.J. van Loo, H. Heijigers, G. Bastin, and W. Sloof, “The Influence of Oxide Surface Layers on Bulk Electron Probe Microanalysis of Oxygen – Applications to the Ti-Si-O System”, *Scanning*, **15** (1993) 165.
26. E.W. Young, J.C. Riviere, L.S. Welch, *Appl. Surf. Sci.*, **31** (1988) 370.
27. U. Bardi, A. Atrei, and G. Rovida, “Initial Stages of Oxidation of the Ni_3Al Alloy: Structure and Composition of the Alumina Oxide Overlayer Studied by XPS, LEIS and LEED”, *Surf. Sci.*, **268** (1992) 87.
28. J.-P. Jacobs, S. Reijne, R.J.M. Elfrink, S.N. Mikhailov, and H.H. Brongersma, “Qauntification of the Composition of Alloy and Oxide Surfaces Using Low-Energy Ion Scattering”, *J. Vac. Sci. Technol. A*, **12** (1994) 2308.
29. C.A. Barret, *A Statistical Analysis of Elevated Temperature Gravimetric Cyclic Oxidation Data of 36 Ni- and Co-Base Superalloys Based on an Oxidation Attack Parameter*, (1992) NASA Technical Memorandom 105934.
30. W.Y. Lee, Y. Zhang, I.G. Wright, B.A. Pint, and P.K. Liaw, “Effects of Sulfure Impurity on the Scale Adhesion Behavior of a Desulfurized Ni-Base Superalloy Aluminized by Chemical Vapor Deposition”, *Metall. Mater. Trans. A*, **29A** (1998) 833.
31. D. Clemens, V.R. Vosberg, H.J. Penkalla, U. Breuer, W.J. Quadakkers, H. Nickel, “TEM and SNMS Studies on the Oxidation Behaviour of NiCrAlY-Based Coatings”, *Fresenius J. Anal. Chem.*, **358** (1997) 122.
32. F.S. Pettit and G.H. Meier, “Processing Issues Related to Environmental Effects in Superalloys, Composites and Intermetallics”, in *Processing and Design Issues in High Temperature Materials*, N.S. Stoloff and R.H. Jones (Eds.), TMS, Warrendale, PA (1997) p.379.
33. J.L. Cocking, G.R. Johnston, P.G. Richards, “Protecting Gas Turbine Components”, *Platinum Met. Rev.*, **29** (1985) 17.
34. P.C. Patnaik, R. Thamburaj, T.S. Sudarshan, “Formation and Behaviour of Platinum Aluminide Coatings on

Nickel-Base Alloys", in: *Surface Modification Technologies III*, T.S. Sudarshan, D.G. Bhat (Eds.), TMS, Warrendale, PA, 1990, p.759.

35. T.N. Rhys-Jones, "Coatings for Blade and Vane Applications in Gas Turbines", *Corros. Sci.*, **29** (1989) 623.
36. R. Streiff and D.H. Boone, "Corrosion Resistant Modified Aluminide Coatings", in: *Coatings and Bimetallics for Aggressive Environments*, R.D. Sisson Jr. (Ed.), ASM, Metals Park, OH, 1985, p. 159.
37. J.C. Schaeffer, "The Effect of Platinum on the Behavior of Diffusion Aluminide Coatings", MS Thesis, University of Pittsburgh, 1987.
38. E.J. Felton, "Use of Platinum and Rhodium to Improve Oxide Adherence on Ni-8Cr-6Al Alloys", *Oxid. Met.*, **10** (1976) 189.
39. E.J. Felton and F.S. Pettit, "Development, Growth, and Adhesion of Al_2O_3 on Platinum-Aluminum Alloys", *Oxid. Met.*, **10** (1976) 189.
40. J.G. Fountain, F.A. Golightly, F.H. Stott, G.C. Wood, "The Influence of Platinum on the Maintenance of α-Al_2O_3 as a Protective Scale", *Oxid. Met.*, **10** (1976) 341.
41. M.R. Jackson, J.R. Rairden, "The Aluminization of Platinum-Coated IN-738", *Metall. Trans. A*, **8A** (1977) 1697.
42. I.M. Allam, H.C. Akuezue, D.P. Whittle, "Influence of Small Pt Additions on Al_2O_3 Scale Adherence", *Oxid. Met.*, **14** (1980) 517.
43. J.H.W. de Wit, P.A. van Manen, "The Precious Metal Effect in High-Temperature Corrosion", *Mater. Sci. Forum*, **154** (1994) 109.
44. C-O. Moon and S-B. Lee, "Analysis on Failures of Protective-Oxide Layers and Cyclic Oxidation", *Oxid. Met.*, **31** (1993) 1.
45. C.A. Barrett and C.E. Lowell, "Comparison of Isothermal and Cyclic Oxidation Behavior of Twenty-Five Commercial Sheet Alloys at 1150°C", *Oxid. Met.*, **4** (1975) 307.
46. B. Gleeson and M.A. Harper, "The Long-term, Cyclic-Oxidation Behavior of Selected Chromia-Forming Alloys", *Oxid. Met.*, **49** (1998) 373.
47. J.H. Sun, HC. Jang, and E. Chang, "Effects of Pretreatments on Structure and Oxidation Behaviour of D.C.-Sputtered Platinum Aluminide Coatings", *Surf. Coat. Technol.*, **64** (1994) 195.
48. G.R. Krishna, D.K. Das, V. Singh, S.V. Joshi, "Role of Pt Content in the Microstructural Development and Oxidation Performance of Pt-Aluminide Coatings Produced Using a High-Activity Aluminizing Process", *Mater. Sci. Engin.*, **A251** (1998) 40.
49. C. Bätzner, "Aluminum-Nickel-Platinum" in: *Phase Diagrams of Ternary Nickel Alloys*, VCH,1990, p.449.
50. R. Mackie, P. Mart, "X-Ray Diffraction Analysis of Ni-Al-Pt Alloys", in *AXAA-88*, Perth, Australia, 1988, p.453.
51. F. Ritzert, D. Arenas, D. Keller, V. Vasudevan, "The Effect of Alloying on Topologically Close Paked Phase Instability in Advanced Nickel-base Superalloy René N6", in *Processing of metals and Advanced Materials: Modeling, Design and Properties*, B.Q. Li (Ed.), TMS, Warrendale, PA, (1998) p.163.
52. B.L. Ferguson, G.J. Petrus and M. Ordillas, "A Software Tool to Design Thermal Barrier Coatings", NASA Contract NAS3-27281 Final Report, 1994.
53. R.A. Miller, "Progress Towards Life Modeling of Thermal Barrier Coatings for Aircraft Gas Turbine Engines" ASME, Paper 87-ICE-18 (1987).
54. G.C. Wang, W. Phucharoen, R.A. Miller, "Finite Element Thermal Stress Solutions for Thermal Barrier Coatings", *Surf. Coat. Technol.*, **32** (1987) 307.
55. Korinko, personal communication
56. F. Gesmundo and B. Gleeson, "Oxidation of Multicomponent Two-Phase Alloys", *Oxid. Met.*, **44** (1995) 211.
57. P. A. Steinmann, H. I. Hintermann, "A Review of the Mechanical Tests for Assessment of Thin-film Adhesion", *J. Vac. Sci. Tech.*, **A7** (1989) 2267.
58. M. R. Begley, D. R. Mumm, A. G. Evans, J. W. Hutchinson, " Analysis of a Wedge Impression Test for

Measuring the Interface Toughness Between Films/Coatings and Ductile Substrates," *Acta Mater.*,(1999) in Press.

59. Flinn, P A; Gardner, D S; Nix, W D, "Measurement and Interpretation of Stress in Aluminum-based Metallization as a Function of Thermal History", *IEEE*, **ED-34** (1987) 689.
60. Q. Ma and D. R. Clarke, 1994, "Piezo-Spectroscopic Determination of Residual Stresses in Polycrystalline Alumina", *J. Amer. Cer. Soc.*, **77** (1994) 298-302.
61. Bastawros, A.-F. and McManuis, R., "Case Study: Use of Digital Image Analysis Software to Measure Non-Uniform Deformation in cellular Aluminum Alloys", *Exp. Tech.*, **22** (1998) 35.

8. Expected Outcomes

The principal expected outcome of the proposed study is to improve the performance and predictability of TBC systems by gaining a more detailed fundamental understanding of the factors governing the reliability and durability of the TGO which develops on an alloy. Essential to achieving this outcome is maximization of Al_2O_3-scale adhesion during long-term exposure. This is dependent upon such factors as: the structure and composition of the oxidizing alloy; the transient oxidation behavior of the alloy; growth rate of the TGO scale; the development and growth rate of physical defects within the scale and/or the scale/coating or substrate interface; the presence of metallic elements other than aluminum in the TGO (*i.e.*, the formation of an inhomogeneous TGO); and the depletion or enrichment of minority elements at the alloy/TGO interface. Thus an additional expected outcome is the attainment of a better understanding of the factors leading to maximized Al_2O_3-scale adhesion. Such an understanding is critically important to improving the durability and reliability of TBC systems.

9. Research Facilities

The following existing research items are available at Iowa State University. Our research philosophy is for graduate and undergraduate students to have intensive hands-on opportunities with state-of-the -are research equipment. Accordingly, with the exception of the JEOL Scanning Auger Microprobe, the equipment below will be operated by the students associated with this program; as required in specific cases, trained operators will work with the students.

JEOL 7830F thermal field emission scanning Auger microprobe equipped with a hemispherical analyzer

Amray 1845 field emission scanning electron microscope

Philips CM30 transmission electron microscope with parallel electron energy loss spectroscopy

JEOL 100CX scanning transmission electron microscope

Optical microscopy with digital image analysis

Philips X-ray generator with powder diffractometer

Perkin-Elmer multi-technique chamber, model 5500 with PHI-ACCESS software (includes X-ray photoelectron spectroscopy and low energy ion scattering)

Ultrahigh vacuum chamber equipped with Varian four-grid low energy electron diffraction optics, single-pass cylindrical mirror analyzer for Auger electron spectroscopy, sputter gun and provisions for gas exposure

Ultrahigh vacuum chamber equipped with an Omicron variable temperature scanning tunneling microscope (50 K – 900 K), sputter gun, a single-pass cylindrical mirror analyzer for Auger electron spectroscopy, and provisions for gas exposure

ARL electron microprobe with computerized stage drive

Thermo Jarrel IRIS inductively coupled plasma atomic emission spectrometer

Horiba EMIA-520 carbon/sulfur analyzer

Leco TC-436 oxygen/nitrogen analyzer

Miller-Thermal 3620 Plasma Spray console with robot-controlled SG-100 gun. 100ft^3 vacuum chamber for reduced-pressure, controlled atmosphere plasma spraying

Research-level high pressure gas atomizer for producing up to 10kg of alloy powders

Buehler Phoenix 4000 automatic polishing unit

Buehler Isomet 2000 precision diamond wafering saw

Bridgman and Czochralski single-crystal growth units

10. Research Team and Collaborating Institutions

Iowa State University (ISU) has assembled a team of scientists from its faculty to collaborate on the various objectives of the proposed project. The ISU team is truly multidisciplinary, consisting of faculty members from the Departments of Materials Science and Engineering, Mechanical Engineering, Aerospace Engineering and Engineering Mechanics, and Chemistry. The members of the ISU team, together with their associated department and areas of specialization relevant to the proposed study are given in the table on the following page.

Professor	**ISU Department**	**Specialization**
[redacted]	Aerospace Engineering & Engineering Mechanics	• Experimental micromechanics • Finite element simulations
[redacted]	Materials Science & Engineering	• high-temperature oxidation • coating/substrate interdiffusion
[redacted]	Materials Science & Engineering	• Electron microscope characterization (analytical and transmission) • experimental, numerical, and theoretical analysis of deformed ceramics
[redacted]	Mechanical Engineering	• development of advanced coatings via plasma-spray techniques • microstructural characterization
[redacted]	Chemistry	• surface structure and reactivity • oxidative corrosion

Each Principal Investigator on the university team has extensive expertise in their respective technical areas. Dr. [redacted] expertise is in experimental micromechanics and computation. He has published over 25 papers on frontier mechanics experiments that tracked highly heterogeneous deformation fields in order to investigate size-scale effects in crystalline solids and layered structures. Dr. [redacted] has published over 60 papers on the corrosion and oxidation of materials, diffusion and protective coatings. He is Associate Editor of the journal *Oxidation of Metals*, and member of the editorial advisory board for *Advanced Engineering Materials*. Dr. Kramer has published over 70 papers on the applications of analytical electron microscopy to intermetallic and ceramic systems. Dr. [redacted] has published over 50 papers detailing the synthesis, processing and characterization of advanced structural materials and novel surface coatings. Dr. [redacted] is currently Chair of the Department of Chemistry. She has over 150 publications related to surface science and is a member of the editorial advisory boards for *Surface Science*, *Surface Science Reports*, *Langmuir*, *Journal of Colloid and Interface Science*, and the *Journal of Vacuum Science and Technology B*.

The university team will interact with researchers at Rolls-Royce Allison (Dr. [redacted]), Cannon-Muskegon (Mr. [redacted]), NASA Glenn Research Center (Dr. [redacted]

[redacted] and Dr. [redacted]), and Oak Ridge National Laboratory (Dr. Peter Tortorelli, Dr. [redacted] Dr. [redacted], and Dr. [redacted]). In addition, Mr. [redacted], formerly of United Technologies and having extensive research experience in the area of advanced TBCs, will interact as a consultant, assisting in the interpretation of results and in the design of experiments. Dr [redacted] is an international leader in the field of TBCs, and he will also assist (via in-kind support) in the interpretation of results and in the design and implementation of experiments. The level of interaction with the other researchers will range from in-kind support or consultation to the sharing of technical information and data from ongoing, compatible studies.

11. Project Coordination

Dr. [redacted] will serve as the Project Coordinator. The Principal Investigators from the university team for the four project objectives are as follows:

Objective	Principal Investigtor(s)
1. *Determination of the chemical and structural factors governing exclusive α-*Al_2O_3 *scale formation*	
Task 1: passive/transient behavior	[redacted]
Task 2: long-term behavior	[redacted]
2. *Optimization of Pt-aluminide coatings*	
• fabrication of tailored structures	[redacted]
• oxidation testing	[redacted]
3. *Coating/substrate interdiffusion*	
• chemical analyses and characterization	[redacted]
• modeling/verification	[redacted]
4. *Determination of mechanical parameters associated with the TGO*	[redacted]

The mail-out of quarterly reports, periodic visits, and the holding of an Annual Participant Workshop at ISU will facilitate interaction between the university team and the external participants.

12. Budget

12.1 Budget Summary

	30 Apr 00 to 29 Nov 00	30 Nov 00 to 29 Nov 01	30 Nov 01 to 29 Nov 02	30 Nov 02 to 29 Apr 03
A. Personnel	172,794	385,160	467,782	196,070
Principal Investigators	50,093	68,217	74,111	20,244
Postdoctoral Associates	49,613	88,962	92,520	38,858
Graduate Students	42,638	175,482	248,650	114,918
Undergraduate Students	30,450	52,500	52,500	22,050
B. Materials/Operating	17,052	47,640	62,541	33,667
C. Equipment	115,000	51,000	6,000	
D. Travel	6,960	12,000	12,000	5,040
E. Publications/Reports	1,160	2,000	2,000	840
F. Subawards	NONE	NONE	NONE	NONE
G. Consultant Fees	3,480	6,000	6,000	2,520
H. Communications	NONE	NONE	NONE	NONE
I. Administration	NONE	NONE	NONE	NONE
J. Overhead	89,643	201,496	244,894	105,971
K. Total Costs	**406,089**	**705,297**	**801,216**	**344,108**

TOTAL FIRST THREE YEARS: **$2,256,710**

	30 Apr 03 to 29 Nov 03	30 Nov 03 to 29 Nov 04	30 Nov 04 to 29 Apr 05
A. Personnel	365,282	476,714	157,134
Principal Investigators	59,640	79,884	13,404
Postdoctoral Associates	96,220	100,070	42,029
Graduate Students	178,972	244,260	79,650
Undergraduate Students	30,450	52,500	22,050
B. Materials Operating	44,333	54,083	19,584
C. Equipment	0	0	0
D. Travel	6,960	12,000	5,040
E. Publications/Reports	1,160	2,000	840
F. Subawards	NONE	NONE	NONE
G. Consultant Fees	3,480	6,000	2,520
H. Communications	NONE	NONE	NONE
I. Administration	NONE	NONE	NONE
J. Overhead	187,441	245,105	82,377
K. Total Costs	**608,656**	**795,902**	**267,494**

TOTAL YEARS 4 AND 5: **$1,672,052**

TOTAL COSTS (5 YEARS): **$3,928,762**

12.2 Budget Justification

(a) Personnel

The proposed study is comprehensive, involving five principal investigators, an outside technical consultant, and key interactions with industry and government laboratories. Included in the personnel budget is support for 9 PhD students, 10 Masters students, 2 postdoctoral research associates, and the part-time employment of 7 undergraduate students for each year of the program.

(b)Materials and Characterization

Objective 1.

The first two years of the program will require extensive alloy preparation and characterization costs. Note that the alloys prepared here will be used in the other components of the program too. Nominally 24 alloy compositions will be studied to span the critical regions of the respective phase diagrams from the systems being studied. Most alloys will be prepared by arc melting together high purity constituents; moreover, each alloy sample prepared will be fully analyzed for composition and structure using ICP-AES, XRD, SEM and EPMA). Note that Pt alloy powders are available at no charge to this program via an ongoing collaboration between Drs. [redacted]. Several specific alloys will be prepared as single crystals using Bridgman methods to augment the UHV oxidation studies of polycrystalline samples.

In Task 1 of this section, passive and transient oxidation studies will require consumable materials for ultrahigh vacuum equipment, heating fixtures and controlled atmosphere gases. Dr. Thiel requires \$6000/student for these materials.

In Task 2 of this section, the isothermal and cyclic oxidation studies will require controlled atmosphere gases and extensive characterization using XRD, SEM,TEM, EPMA and SAM. Dr. [redacted] requires \$5000/student for the oxidation studies and Dr. [redacted] requires \$5000/student to support the TEM and SAM characterization efforts.

Objective 2.

The experiments to prepare tailored microstructures of Ni-Al+Pt coatings using vacuum plasma arc spraying will require high purity plasma gases (e.g., Ar, He and H_2), plasma gun consumables (e.g., anodes, cathodes and gas injectors) and starting powders. Powders will be prepared primarily in-house using gas atomization facilities. In addition to coating preparation, characterization requirements will include extensive metallography and XRD, SEM and EPMA following the planned heat treatments. Dr. [redacted] requires \$6000/student for the vacuum plasma spraying and coating characterization efforts.

Objective 3.

The interdiffusion studies in this section of the program will require substantial analysis by SEM and EPMA. Dr. [redacted] requires $7000/student to support the SEM and EPMA analyses of materials tested in the section.

Objective 4

The evaluation of the TGO mechanical behavior will necessitate fabricating a host of fixtures for holding and loading coating specimens. Dr. [redacted] requires $5000/student to cover the necessary materials and machine shop services.

(c) Equipment

Objective 1.

A magnetically levitated turbopump is required for to eliminate potential oil contamination during UHV studies. ($25,000 in Year 1)

An oxidation furnace will need to be purchased for performing pre-oxidation studies ($10,000 in Year 1)

A CAHN microbalance TGA unit will need to be purchased for controlled atmosphere oxidation studies ($25,000 in Year 1)

Two rigs will need to be fabricated for performing cyclic oxidation tests ($15,000 for two Year 1 and another $15,000 for two in Year 2)

Thermo-Calc and *DICTRA* computer software, each with databases, will be to help model and predict phase equilibria and diffusion behavior ($11,000 in Year 2 and $6,000 in Year 3)

Objective 3.

A controlled-atmosphere furnace will be assembled to perform the required interdiffusion studies ($5,000 in Year 2)

Objective 4.

A residual stress measurement system based on Micro-Raman spectroscopy will be initially fabricated and integrated with the oxidation chamber to monitor the evolution of residual stress during thermal cycling. Preliminary equipment will include laser, optical control elements, detectors and hardware/software control. ($40,000 in Year 1).

A indentation fracture fixture will be fabricated to permit wedge indentation tests using existing tensile testing frames ($5,000 in Year 2)

A digital imaging facility for full-field deformation measurements aimed at qualitative assessment of the spatial distribution of residual stresses with the oxide film. Facility includes high resolution CCD array, digital imaging board, telecentric imaging lenses and computer. ($15,000 in Year 2).

(d) Travel

Domestic travel will include attending 3 scientific meetings per year. We expect that 1 Principal Investigator and 2 graduate students will attend each meeting. ($12,000 per year for 3 meetings at $4,000/meeting for 3 attendees).

(e) Publications

Page charges for multiple yearly publications ($2,000 per year)

(f) Consultant Fees

Mr. Norman Bornstein will collaborate as a consultant. He is a leader in the development and understanding of corrosion mechanisms and has substantial background in gas turbine component design and testing. ($6,000 per year: 30 hours at $200/hour).