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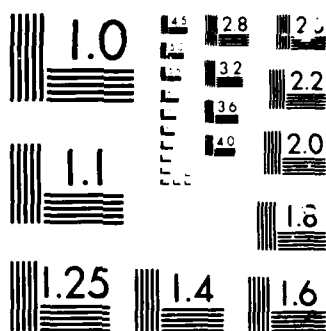
HIGH TEMPERATURE PROTECTIVE COATINGS FOR AERO ENGINE GAS TURBINE COMPONENTS

by

P.C. Patnaik, J.-P. Immarigeon
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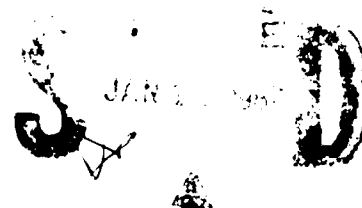National Research   Conseil national
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HIGH TEMPERATURE PROTECTIVE COATINGS FOR AERO ENGINE GAS TURBINE COMPONENTS

REVÊTEMENTS PROTECTEURS HAUTES TEMPÉRATURES POUR COMPOSANTS DE TURBINES À GAZ AÉRONAUTIQUE

by/par

P.C. Patnaik, J.-P. Immarigeon

National Aeronautical Establishment
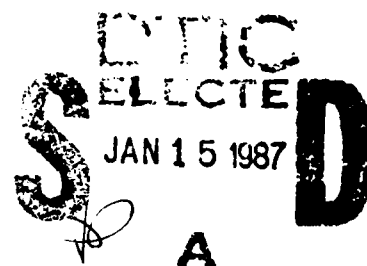
OTTAWA
SEPTEMBER 1986

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ABSTRACT

Aluminide coatings have been widely used in the aircraft industries for the protection of gas turbine engine hot section components against oxidation and/or hot corrosion. This paper considers modes of coating degradation under conditions of cyclic oxidation, hot corrosion and corrosion-erosion interactions during service as well as the effects of interdiffusion between coating and substrate alloys either during service or coating application. It also discusses means of improving existing coatings as well as advanced coating systems currently under development. In assessing coating performance, consideration must be given to the influence coatings may have on substrate properties such as mechanical strength, resistance to creep and resistance to mechanical and thermal fatigue. Finally it is stressed that proven performance for a given coating/substrate combination is no guarantee that no deleterious reaction will occur, when the same coating is used with a different substrate alloy. Therefore, coating substitution requires requalification.

RÉSUMÉ

Les revêtements par aluminisation sont couramment utilisés dans l'industrie aérospatiale pour la protection contre l'oxidation et la corrosion à chaud des parties chaudes de turbines à gaz. On décrit dans ce rapport les modes d'endommagement de ces revêtements sous des conditions d'oxidation cyclique, de corrosion à chaud et sous l'effet combiné de la corrosion et de l'érosion. On considère aussi les effets de l'interdiffusion entre le revêtement et son substrat, soit en cours d'utilisation ou durant la réalisation du revêtement. On discute des moyens disponibles pour améliorer la durabilité de ce type de revêtement ainsi que des avantages qu'offrent de nouveaux types de revêtement en cours de développement. Afin d'évaluer un revêtement, il est nécessaire de prendre en considération l'influence qu'il peut avoir sur les propriétés mécaniques du matériau protégé, et plus particulièrement sur la résistance à la traction, au fluage et à la fatigue mécanique ou thermique. Finalement, on souligne qu'une combinaison revêtement-substrat éprouvée n'offre pas de garantie que le même revêtement n'aura pas d'influence défavorable sur les propriétés d'un substrat différent. Par conséquent, la substitution d'un revêtement pour un autre doit être qualifiée.

CONTENTS

1.0 INTRODUCTION

The technology of coatings for gas turbine hot secton components has evolved to the point when several commercial products are now available that offer reasonable protection against environmental attack to both nickel and cobalt based superalloy components. These coatings are of the diffusion type and are applied mostly by pack cementation techniques. Continued demands for higher turbine inlet temperature beyond normal practice, to improve engine performance and fuel economy, are creating a need for new improved materials capable of withstanding increasingly higher service temperatures. In the case of nickel based superalloys, higher strength at elevated temperature is achieved by reducing the chromium content of the alloy. However, this in turn decreases resistance to oxidation and hot corrosion. There is therefore a need for improved protection against environmental attacks by oxidation and hot corrosion, a challenge currently being met through the development of new generations of advanced coatings.

This report reviews briefly the types of damage that will normally be incurred by hot section components in aero engines and addresses the particular problem associated with surface degradation of coated components. Preventive measures are discussed and the current state of the hot section coating technology is reviewed with particular emphasis on the more advanced diffusion coatings as well as the new overlay and thermal barrier coatings.

2.0 PROBLEMS IN THE HOT SECTION OF AERO ENGINES

In general the gas stream in the hot section of a gas turbine is a highly oxidizing environment. Reducing conditions if present are transient and of a non-equilibrium nature. A summary of the relative severeties of surface and coating degradation of turbine airfoils is presented in Table I[1]. As observed in the table, aircraft turbine airfoils will typically incur severe oxidation, interdiffusion, thermal fatigue and moderate hot corrosion damage during normal service. Severe hot corrosion problems may also be encountered due to increased levels of salt ingestion associated with operations of aircrafts in marine environments. Although in general, the surface degradation of a coating would take place by high temperature oxidation, occasionally augmented by hot corrosion, thermal fatigue cracking initiated in the coating can often be life-limiting. This depends on many factors including design, type of material being used and the severity of the environment, both in terms of service temperature, stresses and the

amount of impurities in the hot gas stream. A summary of conditions prevailing in typical modern gas turbines is presented in Table II[2].

Depending on the service conditions two kinds of undesirable interactions will normally occur: those between the coating and the environment and those between the coating and the substrate. These interactions are discussed below in some detail.

2.1 Interaction Between Coating and the Environment

2.1.1 Corrosion

A review of high temperature oxidation and hot corrosion of alloys used for turbine hot section components has recently been published by one of the authors[3]. Resistance to environmental surface degradation, particularly oxidation and hot corrosion, are the most important factors in selecting a protective coating for a given application. Aluminum based coatings applied by various methods have been widely used in the past because of their superior oxidation resistance, but they do not give the required long-term protection under sulfidizing conditions. This is because the sodium sulfate (formed by the reaction between sodium chloride in the atmospheric air and sulfur in the fuel) reacts with the aluminum oxide on the aluminide coating, forming a non-protective sodium aluminate[8]. If the coating contains sufficient amounts of deleterious elements such as molybdenum or tungsten derived from the substrate (4.2 wt. % Mo in IN713C and 10% W in MAR-M246), acidic fluxing of protective oxide can take place, compounding the problem of hot corrosion. Short term protection is provided by some aluminide coatings if the attack is not too severe. In some cases, aluminide coatings have been found to behave like uncoated blades with no protection at all[5]. This depends on the substrate material which can provide alloying elements through diffusion that will either improve or decrease the coating resistance to environmental attack.

Since Al_2O_3 is the predominant oxide formed on diffusion aluminide coatings, repeated spalling and reformation of alumina due to cyclic oxidation depletes the coating aluminum concentration. This leads to the formation of less protective oxides such as

Cr_2O_3 and NiO in increasing quantities as the aluminum from the coating is depleted until oxidation of the substrate alloy takes place. Cyclic oxidation resistance is found to increase with a decrease in the aluminum content of the base alloy, a trend followed by alloys like IN713C, MAR-M246 and IN738C in this order, at temperatures ranging from 1373K to 1473K[6]. Oxygen active elements (eg. Y, La and Hf), inert oxide particles (eg. Y_2O_3, ThO_2, Hf_2O_3) and precious metals like Pt and Rh have been used to inhibit the spalling of Al_2O_3 from the alloys or coatings[7-10].

The use of chromium or silicon in the coating to control coating/environment interaction and to improve corrosion properties has been introduced commercially in recent years[11,12]. The advantages and disadvantages of such alloying additions will be presented in a later section. Even more recent developments involve the use of complex layers combining the protective action of various elements, although such coatings are not yet available commercially.

2.1.2 Erosion in the Corrosive Atmosphere

Abrasive particles such as sand from the runway can be ingested along with the intake air by aero gas turbines. In addition, not se well documented, so called "hard carbon" particles can be formed under certain condition during fuel combustion in the turbine burners. These particles can cause erosion of the metal or coatings from the turbine airfoils downstream of the burners by solid particle impingement.

The effects of erosion are well documented. It has been shown from weight loss measurements under laboratory conditions that erosion rates vary according to particle velocity, particle size and the angle of impingement[13].

In the presence of corrosive atmospheres, erosion of alloys and coatings has been observed to be more severe than erosion in inert atmosphere[14-17]. In the case of oxidation-erosion, alloys and coatings forming α-Al_2O_3 scales degrade less rapidly than alloys and coatings forming Cr_2O_3 scales. Hot corrosion-erosion is usually more severe than oxidation-erosion or hot corrosion without erosion. It is believed that the mechanism responsible for enhancing hot corrosion in the presence of erosion is related to reductions in the thickness of the porous scale formed on the surface of alloys and coatings, the porous scale being continually abraded mechanically by impinging particles.

2.2   Interaction Between Coating and the Substrate Alloy

2.2.1 Thermal Stability or Interdiffusion

With regards to composition and phase equilibria, coatings should remain stable during service such that the protective elements responsible for oxidation or corrosion resistance are retained by the coating and do not diffuse into the base alloy. However, in practice, diffusion of aluminum takes place from an aluminide coating into the substrate. Similarly, in the case of a silicide coating like NiCrSi, diffusion of silicon into the substrate as well as diffusion of aluminum from the substrate alloy into the coating take place. These reactions have adverse effects on the chemical and mechanical properties of the substrate alloys as will be shown in later sections.

Currently there are two types of aluminide coatings available for turbine blade and vane applications. They differ in the conditions under which they are applied to the substrate by a process known as pack cementation. Processing is done in a low temperature (973K-1173K) high aluminum activity pack and high temperature (1273K-1473K) low aluminum activity pack for the first and second type respectively. The types of microstructures obtained in each case and the mechanism responsible for their formation are illustrated in Figure 1, for the case of a nickel-base superalloy substrate.

The first type of coating is known as an "inward" type. After heat treatment it consists of an external β-NiAl layer in which carbides and all other alloy phases and elements from the substrate are retained, eventually as precipitates if their solubility limit in β-NiAl is exceeded. The second type is known as an "outward" coating. Composition in this case is less dependent on the substrate alloy composition, since the incorporation of substrate alloying elements is limited by their solubility in the β-NiAl phase. The hot corrosion resistance of both type of coatings has been shown to be strongly dependent on the substrate composition due to interdiffusion effects. Smialek et al[23] have shown that interdiffusion between a coating and a superalloy can have deleterious effects on the high temperature oxidation of the coating. Their results on the aluminum concentration profiles in Figure 2 for a low activity aluminized IN100 indicates that a diffusion annealing treatment at 1373K for 300h (to simulate service) decreased the maximum aluminum concentration level in the coating by 40% relative to the as-coated

value. Similar effects were observed when the specimens were exposed to cyclic oxidation conditions (1h cycle) at 1373K for 300h. In this case, the concentration was decreased by 54% and a 10μm surface depletion zone occurred due to oxidation. The cyclic oxidation behaviour of the diffusion annealed specimens was markedly poorer than that of the as-coated specimens (Fig. 3). Goward et al[24] have also observed a significant loss of aluminum from the coating by surface oxidation as well as by inward diffusion into the substrate. Such loss of aluminum will result in a gradual shift of β-NiAl to mixtures of β and γ´ (Ni₃Al) and finally to mixtures of γ´ and γ thereby decreasing the oxidation resistance of the coating.

A study of the high temperature stability of pack aluminide coatings on IN738LC substrate has been conducted by Cooper and Strang[25]. In a low activity type of aluminide coating, they have observed γ´, carbides and platelets of sigma (σ) below the β-NiAl layer. This is because the outward diffusion of nickel and inward diffusion of aluminum produces a zone beneath the NiAl layer which is depleted in nickel and enriched in aluminum, chromium and molybdenum, a situation conducive to the formation of sigma phase or carbides[26]. Further exposure at high temperatures caused the platelet type sigma phase to penetrate the substrate. Strang has reported the presence of extensive sigma phase precipitation at the diffusion/substrate interface of aluminide coatings on IN738LC[27-29]. In a creep rupture study they have observed sigma platelets extending from the coating/substrate interface upto 100μm into the substrate at temperatures of 1023K and 1123K. No deleterious effect of their formation on the creep or low cycle fatigue properties of the substrate material were observed[28,30,31] probably because the thickness of the specimen used in these studies was large relative to the thickness of the regions affected. However, sigma formation in thin wall sections of the more advanced airfoils with intricate internal cooling passages may have deleterious effects on blade mechanical properties. Under certain conditions the sigma phase platelets have been observed to offer an easy path for crack propagation from the coating into the substrate. Lang and Tottle[32] have made similar observation on coated IN738LC specimens exposed for various periods at temperatures up to 1273K. The effect of sigma phase at the coating/substrate interface on the mechanical properties of the coating as well as the substrate alloy is not very clear, however, Strang has suggested that they may be potentially dangerous on the basis of sub-critical crack growth considerations[33].

Recently Pilsner[34] has observed interdiffusion in a diffusion couple consisting of a plasma sprayed NiCrAlZr coating on a MAR-M247 substrate containing tantalum. Annealing the diffusion couple at 1423K in a flowing-argon atmosphere for 200h resulted in a γ' depleted zone in the substrate material to a depth of 150µm. This occurred as a result of Ta diffusion from the substrate to the coating and the strong γ' forming capability of Ta. Therefore, the thickness of the γ' depletion zone in the substrate decreased with increasing Ta concentration. A parabolic plot of this depletion zone as a function of time is shown in Figure 4. This depletion of γ' from the substrate interdiffusion zone may have serious effects on the mechanical property of a turbine component. However, this has not been documented in the literature to any greater extent.

Cobalt based superalloys have 20 to 30% chromium, 5 to 10% tungsten and 0.5-0.6%C with no aluminum. The aluminide coating is a β-CoAl intermetallic usually obtained by using pack cementation in a low aluminum activity pack. Coating growth is ensured by the diffusion of cobalt in the β-CoAl. The aluminizing temperature in this case is usually 323K higher than the one used for nickel based superalloys. The morphology of the aluminide coating on cobalt based superalloys is shown schematically in Figure 5. The coating does not contain an internal zone as in the case of Ni-base superalloys due to the absence of aluminum in the alloy and the initial surface of the component is located near the CoAl coating-alloy interface. The preferential diffusion of cobalt modifies the composition of the substrate alloy which in turn results in the precipitation of a tungsten-chromium carbide near the surface of the component. This carbide is usually in the form of a continuous layer which limits cobalt diffusion from the alloy.

An aluminized cobalt based alloy, FSX-414, exhibited rapid transformation of the β-CoAl layer to α-Co, from the surface and diffusion zone due to oxidation and interdiffusion, respectively and this reduced the effectiveness of the coating after relatively short exposures to high temperatures (1173K) in air[25]. The CoAl coatings are more brittle than the NiAl coatings with a ductile to brittle transition temperature (DBTT) about 523K higher than the nickel aluminides[33].

2.2.2 Adhesion

The coating must adhere to the substrate alloy so that it does not flake off due to mechanically or thermally induced stresses. Diffusion coatings such as aluminides possess higher adherence properties than the advanced overlay type of coatings. In the latter case, high adhesion can be achieved by a proper choice of coating material with respect to the substrate, taking into account of their individual coefficients of thermal expansion.

2.3   Mechanical Properties of the Coating

During service operation, the coating is strained due to thermal and mechanical stress cycles experienced by the substrate component.   The strain in the coating is generated due to a thermal expansion mismatch between the coating and substrate. Residual stress can also be induced as a result of interdiffusion, chemical reactions with the atmosphere and plastic deformation of the substrate.   Under such conditions the coating may crack thereby providing an easy path for the ingress of oxidant from the turbine atmosphere to the substrate alloy.   It has been suggested[35] that thermal expansion mismatch between the coating and the substrate should be kept below 2×10^{-6} $°C^{-1}$ if excessive strains and stresses are to be avoided during normal service.   Worst situations occur in the case of turbine blades when the thermal expansion coefficient of the coating is greater than that of the substrate alloy[36].   Oxides have lower thermal expansion coefficients than metals or intermetallic phases (Table III) so that compressive strains are always produced in an oxide layer after cooling from the temperature of formation or processing[37].   The greatest strain in this case develops when the interface between the oxide and the substrate remains flat.   Also, factors such as coating thickness and service temperature must be taken into account when considering the ability of the coating to accomodate thermal strains and protect the base material[33,38].

Diffusion aluminide coatings have fairly high ductilities above a certain temperature, known as the ductile/brittle transition temperature (DBTT).   Below this temperature the coating behaves in a brittle manner and is likely to fail in service under the action of severe thermal stresses.   Above this temperature, the coating ductility increases rapidly.   The characteristics of pack aluminide coatings have been shown to be dependent on the coating process, their heat treatment route and to some extent on composition.   Goward[39,40] has demonstrated that a reduction in aluminum content from 32 to 25 wt.% lowers the DBTT of the β-NiAl coatings by more than 373K.   Similarly,

alloying the NiAl with other elements like platinum has been observed to have an effect on the DBTT of the coating[41]. The DBTT of overlay type of coatings are also dependent on their chemical compositions and for example can vary from room temperature to 1073K in the NiCrAlY coatings[42].

Coating thickness also has an effect on the DBTT of coatings. This has been demonstrated by Wahl et al[43] in studies carried out on chemically vapor deposited (CVD) silicon-boron and titanium-silicon on an IN738LC substrate. In these tests it was shown that increasing the thickness of silicon boron coatings from 50μm to 180μm raised the DBTT by more than 473K and the addition of titanium to silicon coatings raised the DBTT from 823K to approximately 1173K. These features and the effects of substrate composition on the DBTT are illustrated in Figure 6. The ductility of an aluminide coating has also been observed to increase at a given temperature as the coating thickness decreases[44]. Finally, it should be noted that since diffusion type coatings are metastable by nature, their composition, structure and mechanical properties will change with thermal exposure during operation in the turbine. Therefore, a change in their DBTT might therefore be expected during survice.

On the basis of these observations, it is apparent that the most important mechanical property of a coating must be its resistance to thermo-mechanical induced cracking. The likelihood of premature mechanical failure of both coating and substrate can be minimized by[38]:

(a)   making the coating as thin as practically possible, without compromising its effectiveness as a protection against corrosion,

(b)   selection of coatings with high inherent ductilities and/or low DBTT,

(c)   minimization of thermal expansion coefficient mismatches between the coating and the substrate,

(d)   reducing thermo-mechanical strains below the DBTT by carefully controlling the turbine start-up and shut-down cycles.

2.4 Effects of Coating on Substrate Alloy Properties

Protective coatings can have negative effects in a variety of ways on the properties of base materials. As discussed in previous sections, interdiffusion can alter the composition of the substrate material and hence its properties during either service or application. In particular, since application of coating involves much higher temperatures, undesirable precipitation of deleterious phases may occur in the substrate. This may lead to a deterioration of creep and ductility properties of the substrate material. Similar effects on the substrate alloy may be obtained if an improper heat treatment cycle is chosen for the coating/substrate combination. Finally, brittle coatings may develop fine cracks during their application and these may propagate by low cycle fatigue or high cycle fatigue into the base metal. In assessing the suitability of a particular coating for a given substrate, coating-substrate interactions and their effects on time independent properties such as tensile and impact properties as well as time or cycle dependent properties such as creep and fatigue resistance should be considered.

2.4.1 Tensile and Impact Strengths

The effects of coatings on the tensile properties of various nickel and cobalt based superalloys have been investigated by a number of workers[45-48]. It has been shown that tensile properties determined in the temperature range 298K-1273K are only marginally affected provided that a suitable post-coating corrective heat treatment is carried out[45]. In some cases, no post-coating heat treatment was necessary as no significant difference between coated and non-coated material was found[43]. Low pressure plasma spray of MCrAlY type coatings on IN738LC substrate tested in the as-coated condition at room temperature and 923K has also demonstrated no reduction in tensile properties[46,47]. However, a loss of tensile strength was observed by Kaufman[48] in thin sections of coated nickel based superalloys.

Effects of CVD TiSi coating on impact properties of Hastelloy-X have been determined by Wahl et al[46]. Impact testing of this material has indicated that the cooling phase of the heat treatment associated with the coating process was too slow which caused a loss in impact strength.

Therefore in general, it can be said that the coatings do not effect the tensile and impact strength properties directly, although, the associated coating thermal processes can lead to a significant reduction in strength. The extent of this effect is much more pronounced in the pack diffusion processes rather than in overlay processes. This loss of strength can be generally compensated by a suitable post-coating treatment. Thin sections of superalloys have demonstrated a loss in tensile strength due to the application of a coating.

2.4.2 Creep and Stress Rupture Strength

Creep of a material is mainly a bulk process. The application of a coating can influence creep through any of the following processes[37]:

(i)   heat treatment due to the coating process,

(ii)   long range residual stresses in the substrate,

(iii)   crack initiation due to the coating starting from the surface or the coating-substrate interface,

(iv)   diffusion of coating elements into the base metal, and

(v)   diffusion of base metal elements into the coating.

With the exception of the first factor, all other coating effects are more pronounced in the thin-walled internally cooled turbine airfoil. As a long-term effect, reduction in stress rupture properties of thin sections has been observed in chromized and aluminized unidirectionally solidified IN738LC[37], aluminized René 80, René 120[48] and aluminized Nimonic 105[49]. On the other hand, creep rupture properties of IN738LC have not been found affected to any great extent by coating[38,50]. However, Pt-Al coatings on IN738LC have deteriorated the stress rupture properties of the base material due to the formation of brittle phases at the coating substrate interface[45]. In corrosive environments, coatings may have positive influences on the stress rupture properties by reducing the corrosion or oxidation attack from the environment[44,51].

2.4.3 Fatigue Strength

A wide variation in results have been reported on effects of aluminide coatings on the low cycle, high cycle and thermal fatigue properties of nickel and cobalt based superalloys. Since fatigue failures are generally initiated at the surface, in the absence of internal defects and porosity, coating may potentially effect fatigue properties of coated components. If coating properties such as yield strength, thermal expansion, ductility and DBTT are significantly different from those of the substrate, then cracks can be generated in the coating and the ability of the coating to protect the substrate material from corrosion will be lost. Such cracks may propagate into the substrate and lead to premature failure of the entire component. On the other hand, if the coating has better fatigue properties than the substrate, an improvement on the overall behaviour can be expected even in a severe corrosive environment.

These are three types of fatigue failure modes normally encountered in a gas turbine engine:

(a)   Low Cycle Fatique

Effects of coatings on the low cycle (high strain) fatigue have been reported by few workers and they vary considerably depending on the coating/substrate alloy system. Bartocci[52] has shown that higher thicknesses of aluminide coatings on SEL 15 has lead to lower fatigue lives while Wells and Sullivan[53] have shown that an aluminide coating has improved the LCF resistance of U700. The results obtained by Strang[29] on the LCF strength of IN738LC at 923K and 1023K have indicated that there is little difference in the properties of non-coated and coated material. From the summary of various test results reported in reference[38] it can be concluded that a coating has no adverse effects on the low cycle fatigue properties of nickel and cobalt based superalloys in cases where it has good plasticity above the DBTT and below a critical coating thickness.

(b)   High Cycle Fatigue

Various workers have reported the results of limited studies indicating that the use of coatings can have both positive and negative effects on the high cycle (low strain)

fatigue properties of base materials[54-59]. The dependence of HCF properties of U500 on coating thicknesses has been reported by Betts[54], who found that, the higher the thickness the lower was the HCF strength. At coating thicknesses greater than 60μm, premature failure of the aluminide coating has been observed as a result of cracking in the coating layer[55]. In contrast, improvements in the room temperature fatigue properties of aluminide coated nickel and cobalt based alloys have been reported by Puyer[56] as well as Lane and Geyer[57]. When HCF and hot corrosion are acting concurrently the coating is expected to give a beneficial effect by protecting the surface from accelerated crack initiation[59].

(c)   Thermal Fatigue

Materials in high temperature environments are subjected to thermal strains resulting from rapid temperature changes. For example the thin trailing edge of a gas turbine blade has been shown to heat up and cool down faster than the bulk *during service condition.* The transient difference between these temperatures (Table II) gives rise to cyclic thermal strains which reach maximum at the thin edge.

When the thermal strains are relatively severe, the protective barrier provided by the coatings may lose integrity due to thermal shock or fatigue. Because the coating and superalloy substrate are sometimes mechanically incompatible, significant mismatch strains can develop in a coating/alloy system during thermal cycling. These tensile or compressive thermal expansion mismatch strains can increase or decrease the coating strain. An increase can lead to cracking of the coating which then becomes the starting point for corrosion attack and failure. Selection of coatings for each applicaton must therefore be based not only on their corrosion resistance but also on their DBTT and compatibility with the substrate alloy in terms of their thermal expansion properties (Table III). Thermal fatigue properties of materials can be determined by either using gas[61] or plasma torches[62], fluidized bed facilities[60,63-71] or burner rigs[67].

Thermal fatigue properties of a number of nickel and cobalt based superalloys with inward and outward types of diffusion aluminide coatings have been investigated by Boone and Sullivan[72]. These results have indicated that in polycrystalline substrates, inward-type aluminide coatings generally improved the fatigue performance while the outward-

type was detrimental. However, ranking of these two types of coatings on nickel based superalloys were on the basis of crack initiation but not crack propagation, the latter being slower in the columnar grains of outward-type coatings. Further research in this field with well defined strain/temperature/time cycles has shown that outward diffusion type of aluminide coatings possess superior thermal fatigue properties compared to the inward-type[155].

Rairden et al[73] have indicated that due to their good strength and ductility, the low pressure plasma spray (LPPS) coatings of the NiCoCrAlY type are able to retard rack initiation due to thermal fatigue. Coatings on DS-alloys generally do not improve thermal fatigue properties significantly since the DS-alloys as such are superior than their polycrystalline counterparts with respect to thermal fatigue resistance[74,75]. Where coatings led to an improvement of thermal fatigue strength, once a crack initiated its propagation rate was in general greater than those observed in the uncoated material[71].

3.0   RECENT ADVANCES IN COATINGS ON SUPERALLOYS

In general, one may be able to choose a coating for the hot section of gas turbines from essentially three classes of coatings. These are the diffusion coatings, the MCrAlY (M = Ni, Co) overlay coatings and the thermal barrier type of coatings. The various factors that would govern the choice of a coating for particular application were discussed in the previous section. In the following section recent advances in the development of these three classes of coatings are described.

3.1   Diffusion Coatings

There are two processing methods for diffusion coatings; slurry-fusion and pack cementation with the latter process in predominant use. In slurry-fusion processes, a emsion of the coating element or alloy is sprayed or dipped onto the substrate alloy to trolled thickness and further heat treatment in the range (1143K-1368K) gives rise to or mation of a diffusion coating. Part of the coating formation process may also e f sion of the slurry and subsequent solid state diffusion. In the pack cementation parts to be coated are immersed in a powder mixture of the coating element or an activator such as ammonium halide and an inert diluent.

3.1.1 Aluminide Coatings

Aluminum or aluminum alloys have been used to prepare diffusion aluminide coatings. Depending on the nature of the coating material, diffusion heat treatments are given in the range of temperatures 1143K to 1366K for 2 to 24 hours. Post coating heat treatments may be required for some alloys to further diffuse the coating and to develop acceptable microstructures in the base material. Two types of aluminide coatings known as the "inward" and "outward" type can be obtained as discussed in Section 2.2.1.

Numerous attempts have been made to improve the oxidation and hot corrosion behaviour of aluminide coatings[77-82]. A moderate increase in resistance to hot corrosion at intermediate temperatures (1088K-1198K) has been achieved by increasing the chromium concentration of the aluminide coating over that normally desired from superalloy substrate[52,77-79,82]. This has been accomplished either by a chromizing process such as pack cementation or electroplating prior to aluminizing or by a single stage co-deposition of Cr and Al[79-81]. In such coatings, due to low solubility of Cr in NiAl, chromium rich interlayers such as CrNi are formed beneath the NiAl. The interlayers have low diffusivity of Al and hence retard diffusion towards the interior of the alloy[82].

Alloying β-NiAl with 10 a/o Cr has significantly improved the hot corrosion properties of aluminide coatings[83]. Oxidation studies of NiAlCr alloys[84,85] have established that the critical aluminum level needed for forming Al_2O_3 at 1273K is

progressively decreased from approximately 40 a/o Al in binary NiAl to ≃ 15 a/o Al when only 5 a/o Cr is present in the alloy. This is in agreement with the thermodynamic properties of the NiAlCr system in which, chromium, when added to NiAl alloys is known to increase the aluminum activity appreciably[83]. The overal degradation mechanism of an aluminide coating with or without chromium addition can be illustrated using the NiAlCr phase diagram at 1123K. The nickel rich part of the NiAlCr phase diagram at 1123K is shown in Figure 7. Point A on this diagram represents the uncorroded pure β-NiAl composition and point B represents the NiAl composition containing 10 a/o Cr. The change of gross alloy composition as a result of loss of Al through oxide spallation and/or interdiffusion is indicated schematically in each case by arrows originating from points A and B. Although the arrows give a simplified picture of the alloy degradation process, it is clear that for any given amount of Al loss, more of γ´ phase is likely to appear in pure β-NiAl than in NiAl containing 10 a/o Cr. It appears, therefore, that Cr tends to suppress γ´ formation and promote α stability. Since γ´ is particularly susceptible to hot corrosion and α is not, Cr appears to play a most desirable role.

Nickel aluminide coatings have been shown to undergo martensite transformation on rapid cooling from high temperature, a situation leading to an appreciable change in volume[83]. Although the real implications of martensitic transformations on corrosion behaviour of bulk β-NiAl or β-NiAl coatings is not yet fully understood[77], the addition of chromium (∼3 a/o) to β-NiAl has been observed to suppress the martensite transformation and therefore eliminate any detrimental effect. Chromium has a limited solid solubility in β-NiAl (16 a/o at 1273K), therefore any amount in excess of this would precipitate as a second phase which is deleterious to high temperature (1273K to 1373K) oxidation resistance[40].

Another method for coating nickel and cobalt based superalloys known as Allison Electrophoretic Process (AEP) has been developed by the Allison division of General Motors. In this method, a coating is deposited electrophoretically on a turbine component and then the coated article is subjected to thermal diffusion treatment for times necessary to produce substrate coatings with the desired structures[86,87]. Coatings of NiCrAl (AEP-32) and AlCr (AEP-100) have been applied to nickel and cobalt based alloys to overcome thermal cracking and hot corrosion problems[88,89].

Attention has also been given to alloying β-NiAl coatings by silicon[90,91]. Cyclic oxidation and hot corrosion data have shown that a high purity silicon slurry spray followed by a pack aluminizing treatment greatly improved the high temperature oxidation and hot corrosion resistance of nickel based superalloys[90]. Significant improvements on thermal fatigue properties have also been achieved in these cases. A slurry of aluminum-silicon (sermalloy J) was applied to IN738[92], U520 and X45[91] respectively nickel and cobalt based superalloys. Although in general the corrosion behaviour of sermalloy J was satisfactory on all these alloys, partial flaking off the sermalloy J coating was observed on U520 alloys. The main disadvantage of silicon addition to the β-NiAl coating is that it reduces the ductility of the coating. Plasma spray of a NiCr alloy combined with either Cr or Al pack cementation or with AlSi slurry coating has exhibited excellent corrosion resistance under cyclic hot corrosion as well as excellent adhesion under cyclic thermal shock conditions[91].

Improvements in the properties of diffusion aluminides have also been achieved by incorporating noble metals such as platinum and rhodium[93-101]. The concept of the platinum aluminide coating system was first developed by Lehnert with the original British patent issued in 1970[93]. The first commercial coating system LDC-2 was developed by Lehnert and Meinhardt[94]. This coating was produced by initially electrodepositing a platinum layer less than 10μm thick on to a nickel base alloy and subsequently aluminizing the platinized component for several hours at approximately 1323K. The platinum forms an aluminide of $PtAl_2$ and remains concentrated towards the surface regions of the coating. Thus the reaction of aluminum with the oxidation, hot corrosion atmosphere is decreased due to decreased activity of aluminum occurring as a result of platinum addition to the coating.

A modified version of LDC-2 known as RT-22 has been described by Seeling and Stuber[95] which exhibits a two phase microstructure of (NiPt) Al and $PtAl_2$. Another type of Pt aluminide coating developed at Johnson Mathey, designated JML-1 used the fused salt platinum technique to deposit the platinum layer followed by a high activity - low temperature aluminizing treatment. This coating has a thick Pt_2Al_3 outer layer over a duplex $(NiPt)_2Al_3$ + PtAl structured zone[96]. American based companies like Chromalloy, Howmet and Coating Technology Corporation have been producing their own platinum aluminide coatings.

Hot corrosion and oxidation properties of these coatings on nickel and cobalt based superalloys (IN738, IN713 and X40) have been evaluated by various workers[97-100]. All the platinum aluminide coatings exhibited better high temperature oxidation properties than the conventional aluminides. High platinum coatings like JML-1 have better hot corrosion resistance than other low platinum LDC-2, RT-22 coatings[100]. Excellent oxide/coating adhesion is achieved in these coatings[101]. As far as mechanical properties of the coating are concerned, no significant improvement in the thermal fatigue strength can be achieved because these coatings are still based on intermetallic compounds produced by diffusion processes.

It is well known that corrosion resistance of superalloys is much improved by the addition of small amounts of rare earth elements like Y and Hf[8-10,102-105]. Ion plating of yittrium with subsequent pack aluminization has shown much improvement in the oxidation and moderate improvement in hot corrosion resistance of nickel based superalloys. A recent investigation by Jones et al[106] has shown that hafnium is a better candidate than yittrium for low temperature hot corrosion resistance of coatings on nickel and cobalt based alloys. Improvements in oxidation and mechanical properties of the aluminide coatings have been observed by incorporating Al_2O_3 into the coating by a slurry treatment[107].

3.1.2 Chromizing

Chromium diffusion coatings have been used for the protection of iron, nickel and cobalt based alloys. Diffusion chromizing processes have been developed by pack cementation processes[108-110]. The use of this coating to increase the service life of aero gas turbine blades and particularly land based stationary turbine blades have been to protect these materials from high temperature corrosion attack[111-115]. The protective mechanism of chromium diffusion coating is derived from the ability of the coating to develop a dense, coherent oxide Cr_2O_3, as a diffusion barrier against further oxidation, sulfidation and hot corrosion[77-82]. The use of chromium diffusion coating alone is limited in aero gas turbines due to the excessive volatilization of Cr_2O_3 to CrO_3 at temperatures greater than 1223K[84,116-118]. Several chromium diffusion coatings are now available commmercially (Table V) for application at temperatures less than 1223K.

3.1.3 Siliconizing

Thirty years ago it was reported that combination of silicon and chromium as oxide forming elements exhibits a striking improvement against high temperature oxidation and hot corrosion[119,120]. Research on silicon diffusion coatings to protect gas turbine materials from oxidation and hot corrosion has now reappeared[121-126]. The protective effect of this type of coating is due to the formation of a Ni_2SiO_4 scale with a chromium oxide sublayer[127]. Although the corrosion resistance of siliconized blades were superior it is recognized that siliconized coatings are very brittle and evidence of early spalling has been observed in most cases[125-128]. Also, in silicon diffusion coatings on nickel based superalloys, NiSi can form a eutectic with Ni_2Si or $NiSi_2$ (melting point 1238K)[124]. To overcome these problems, overlay coatings with NiCrSi alloys of defined composition have been used that are applied by a reaction sintering process[125,129]. These coatings have shown great promise at 1273K as protective layers for nickel based superalloys with improved oxidation and hot corrosion resistance. Much of this work is in a research stage.

A summary of advantages and disadvantages of various types of diffusion coatings is presented in Table IV. The best coating could be one that combines two or more alloying elements among chromium, platinum and silicon that have been shown individually to improve oxidation and/or hot corrosion resistance of aluminide coatings. In this respect, the particular combination may depend on the substrate alloy for which the coating is intended.

3.2 Overlay Coatings

The overlay coatings developed during the 1970's were most often alloys of Ni(Co, Fe), Cr, Al and Y (MCrAlY type)[130-138]. These overlay coatings applied by electron beam vapour deposition[132-134], plasma spray[135-137] or sputtering techniques[138] allow the coating composition to be designed independent of the substrate alloy. By optimizing the overlay coating composition the best compromise of oxidation resistance, sulfidation resistance and mechanical properties can be made. Excellent thermal fatigue and oxidation-corrosion resistances have been achieved with these overlays compared to the usual diffusion aluminides[73].

CoCrAlY overlay coatings have been found to have much better hot corrosion resistance than the corresponding NiCrAlY coatings in the temperature range 1123-1173K[130]. In the low temperature range 873K-973K, NiCrAlY coatings have been found to be better than the CoCrAlY coatings[131]. A display of the role of the Al and Cr in the chemistry of diffusion and overlay coatings with respect to their oxidation and hot corrosion resistance is illustrated schematically in Figure 8. Superior performances of NiCoCrAlY, CoNiCrAlY and CoCrAlY overlay coatings in both oxidation and hot corrosion environments have encouraged their use in a variety of gas turbine material applications. Another advantage of the overlay coating is that contrary to the diffusion coatings, overlay coatings do not consume the substrate material (Fig. 9). This is important for the repair of the turbine components. For example if a 60μm thick aluminide coating which has penetrated the substrate material by 25μm (in the case of low activity type) is stripped from the blade having a wall thickness 0.5 to 1 mm, a 2 to 5% reduction in the cross-section of the airfoil occurs with a corresponding increase in the net section stress[94].

Silicon has been proven to improve hot corrosion properties of superalloys and MCrAlY coatings[121-126,130]. A recent investigation on the optimization of coating composition for turbine blades has shown that two layers, an inner layer of MCrAlY and an outer layer of silicon modified MCrAlY, resist the high temperature oxidation and hot corrosion significantly better than a simple MCrAlY type of coating[139]. Rairden[132] has shown that a duplex coating of a CoCrAlY overlay with a conventional pack aluminizing is much more resistant to hot corrosion than corresponding NiCrAlY + pack aluminizing coatings.

To resist high temperature oxidation in the range 1273K to 1423K, the most advanced coating has been an overlay of NiCoCrAlY with compositon (in wt.%) Ni-23Co-18Cr-12Al-0.5Y. This coating applied by an EB-PVD process has proved to be useful for the protection of aircraft engine blade airfoils fabricated by directional solidification of the superalloy MM-200 + Hf[130]. An optimized LPPS coating of Ni-20Co-18Cr-12.5Al-0.4Si-0.25 Hf has been shown to provide best performance on a PWA 1480 single crystal alloy[135]. In this work no complete explanation of the beneficial effects of silicon on oxidation resistance of MCrAlY coatings has been provided.

The DBTT characteristics of MCrAlY coatings are dependent on their composition. Boone[42] has shown that in CoCrAlY coatings, aluminum content has a large effect, with high aluminum contents ($\sim$13%) resulting in high values of DBTT and vice versa. Also high Cr levels in these coating alloys favour higher DBTT values, while addition of nickel lowers the DBTT considerably (Fig. 10). Another feature of high nickel MCrAlY coating alloys is that their ductilities are on the whole higher over the whole temperature range, from room temperature to 1073K (Fig. 10).

It is worth mentioning that most of the overlay coating compositions selected for testing and evaluation are generally derived from prior experimental observations. Based on these empirical results of beneficial elements, coating development has continued at an accelerated rate due to the relative ease of application of these coatings by a cheaper and more efficient low pressure plasma spraying process[130].

3.3 Thermal Barrier Coatings

Currently there has been a considerable interest in the use of insulating ceramic thermal barrier coatings (TBCs) to protect hot section turbine components from oxidation and corrosion[149-148]. The thermal barrier coatings have low thermal conductivity and therefore limit the heat flow into the component materials. Materials considered as TBCs are in general oxides such as ZrO_2, Al_2O_3, $CaTiO_4$, $CaSiO_4$, $MgAl_2O_4$ but carbides and nitrides have also been used[149].

ZrO_2 has been used as the base material of TBCs mainly because of its physical properties, such as low thermal conductivity ($\sim$ 1.7 W m^{-1}K^{-1}), high melting point (T_m = 2983K) and moderate thermal expansion ($\sim$ 9 $\times$ 10^{-6}mm^{-1}K^{-1}). Stabilization of cubic ZrO_2 is achieved by addition of other oxides such as Y_2O_3, MgO or CaO[141]. Best thermal shock resistance and properties of ZrO_2 TBCs have been achieved by adding 6 to 8 wt.% Y_2O_3[142]. The major difficulty in the use of these ceramic coatings on metallic (Ni or Co based) turbine components is the most important component is the control of ceramic cracking. The low thermal expansion coefficient of these ceramic coatings and relatively poor mechanical properties result in adhesion and strains which encourage the generation of stresses within the coating which eventually result in spalling[143]. For this reason these coatings are put on the metallic surfaces, perform microcracking and

columnar structures with grain boundaries to the substrate surface (known as coating segmentation) has also been observed. To improve ceramic coating-substrate adhesion and minimize the thermal expansion mismatch between them, graded layers or bond coats and cermets have been used[143,144]. A typical example of a thermal barrier coating with good high temperature properties is ZrO_2-$8Y_2O_3$/Ni-16Cr-5Al-0.15Y[144] and is illustrated in Figure 11.

The behaviour of TBCs in hot corrosion atmospheres has been studied recently[145-150]. Two potential failure modes have been postulated[151]. The saturation of coating porosity with molten salts, resulting in failure by mechanical effects of solidification, melting and hot corrosion by molten salt deposits. Studies on hot corrosion of Y_2O_3 stabilized ZrO_2 has shown a selective removal of Y_2O_3 by the acidic Na_2SO_4-SO_3 melt[152]. The exact mechanism of such degradation phenomenon and its practical significance has yet to be established. Additional life improvements of the TBCs have been achieved by improving the oxidation hot corrosion resistance of bond coatings (NiCrAlYS)[153]. Although improvements by increasing the density of plasma sprayed bond coatings have been obtained[154], much more research in the area of durability testing and evaluation of this class of coating is required.

4.0   SUMMARY AND CONCLUSIONS

Aluminide coatings have been most commonly used in the aircraft gas turbine applications such as blades and nozzle-guide vanes to resist high temperature corrosion. These coatings provide very good oxidation resistance in the gas turbine atmosphere but do not have sufficient resistance to hot corrosion. Therefore in examining the overall role of coatings in prolonging component lives, their advantages and disadvantages must be considered, specially with respect to the diversity of substrate materials. The properties of coatings with respect to oxidation and hot corrosion resistance, overall thermal and structural stability, and more importantly their effect on the mechanical properties of the substrate such as creep and fatigue strength must be considered.

From a coating degradation point of view diffusion aluminides perform a satisfactory role in relatively clean environments, especially on alloys which have moderate resistance to many forms of hot corrosion. Since most of the current

superalloys have inadequate hot corrosion resistance because of their low chromium contents, improvements in the chemistry of diffusion aluminide coatings have taken place by incorporating Cr, Pt or Si in the coating to provide a greater resistance to sulfate induced hot corrosion. For higher temperature or more aggressive corrosion environments, overlay coatings based on MCrAlY(M = Fe,Co,Ni) and MCrSi(Al)Y applied by electron beam evaporation or plasma spray, are suitable for many applications. Depending on the composition, these coatings can have lower DBTT values than other types of coatings and therefore offer the best compromise in terms of oxidation-corrosion resistance and mechanical compatibility with the underlying substrate.

The use of thermal barrier coatings introduced in the early 1970's, particularly for the combustion chamber of aero gas turbines has now been extended for the first stage turbine vane and blade applications. These coatings are based on ZrO_2-Y_2O_3 ceramic materials. The control of spalling of this type of coating has been observed to be a major difficulty although this has been overcome by using different types of bond coats. A typical example of a TBC with good high temperature properties is ZrO_2-$8Y_2O_3$ with a Ni-16Cr-5Al-0.15Y bond coat. The performance of these coatings is governed by various complex factors. Extensive studies on the testing, evaluation and qualification of these coatings on actual turbine components is still under progress.

5.0 ACKNOWLEDGEMENTS

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Table I   Comparison of Surface Related Problems
for Gas Turbine Hot Section Components
as a Function of Applications(1)

	Oxidation	Hot Corrosion	Interdiffusion	Thermal Fatigue
AIRCRAFT	S	M	S	S
UTILITY	M	S	M	L
MARINE	M	S	L	M

L-Light,   M - Moderate,   S - Severe

Table II

Levels of Loading Expected on Gas Turbine Blades in Aircraft Applications[2]

Type of Loading	Magnitude	Effect
a) THERMAL		
Temperature range:		
in combustion gas	up to 1673K	Diffusion Process
in material	up to 1323K	Changes in Structure
local	up to 473K/mm	
Temperature gradients (time-wise)	up to 373K/s	Mechanical Stress
b) MECHANICAL		
Centrigugal stress	170 N/m^2	Cyclic Strain
Stress gradients due to difference in temperature and pressure	±30N/m^2	Formation of cracks in the coating
Gas Velocity	up to 600 m/s	Stripping of the coating, erosion
Foreign Object Impact		Spalling of the Coating
c) CHEMICAL		
Excess Oxygen	12% by volume	Oxidation and corrosion
Contamination in the fuel e.g. S	0.3 w/o permissible 0.1 w/o usual	Alloy degradation by sulfidation
Contamination of the intake air e.g. sea salt, industrial atmosphere	up to 1 ppm	Roughening of the surfaces
Pressure	up to 25 bar	
Flow rate	up to 600 m/s	
Resident time in the gas turbine	5 to 6 ms	

Table III

Thermal Expansion of Coatings and Materials (37)

Material	Temperature Range (°C)	α (x 10-6°C-1)
Metals		
Ni	25-1000	17.1
Co	"	18.45
Cr	"	11.0
Alloys		
Ni-20Cr	20-1000	18.1
IN738LC	20-900	15.7
IN939	20-1000	17.3
X-40	20-980	16.6
A286	20-700	18.0
Intermetallics		
NiAl	250-1050	14.3
Ni_3Al	250-1050	11.9
Ni_3Si	770-1070	14.0
Ni_2Si	870-1070	11.0
Oxides		
Al_2O_3	200-1000	8.0
Cr_2O_3	25-1000	8.0
SiO_2 (Vitreous)	20-1250	0.5
(Quartz)	25-1000	14.6
NiO	20-1000	17.1
$NiAl_2O_4$	25-1000	8.4
ZrO_2 - 5% CaO	"	9.5
Al_2O_3 - ZrO_2	200-1000	7.4

Table IV

Advantages and Disadvantages of Various Types of Diffusion Coatings

	ALUMINIZING	CHROMIZING	SILICONIZING
Phase(s) Responsible	NiAl	Ni-Cr solid solution with α-Cr precipitates	NiSi
Oxidation Properties	- Al_2O_3 former - Excellent for high Temp.Oxid.	- Cr_2O_3 former - Good for high Temp.Oxidation	- SiO_2 former - Very good for high Temp.Oxid.
Stability of Oxide	- Excellent	- Cr_2O_3 forms volatile CrO_3 at T 950°C	- Good
Oxide Spalling	- Severe	- Protective	- Moderate Spalling
Maximum Temperature in use	- 1473 K	- 1223 K	- 1223 K
Hot Corrosion	- Poor hot corrosion resistance. Al_2O_3 dissolved in Na_2SO_4 forming non protective $NaAlO_2$	- Good hot corrosion resistance	- Excellent hot corrosion resistance
Interdiffusional and Phase stability	- Severe interdiffusion of Al into the substrate	- Moderate interdiffusion	- Severe interdiffusion therefore embrittlement of the substrate
	- Enrichment of Al in the diffusion zone favouring sigma phase formation	- Presence of Cr is very much favourable for sigma phase precipitation	- NiSi can form a low melting eutectic with Ni_2Si or $NiSi_2$ (m.p. 965°C)
Thermal Shock Resistance	- Poor	- Good	- Very poor
Mechanical Properties	- Brittle, poor	- Moderate	- Brittle, very poor

Modified Coatings

- Alloying NiAl with
  Cr, Si

  - Use of chromizing as
    a pretreatment

    - Reaction sintering
      of Ni$_6$Cr$_2$Si$_2$
      silicon rich coating

- Using pretreatments
  like chromizing

  - chromaluminizing,
    a process in which
    Cr and Al are codeposited

    - More research is
      being carried out
      on these coatings

- Using rarearth elements
  like Y, Hf to
  improve oxide spalling

- Using noble metals
  like Pt, Rh to improve
  hot corrosion properties

Table V

Commercial Hot Section Coatings available in Canada

Vendor	Source	Coating	Type and Process	Use or application
TMT (Turbine Metal Technology)	Calgary	KS 136	Silicon carbide dispersed aluminide coating	1338 K
		KS 138	Aluminum Oxide dispersed aluminide coating: Al_2O_3 slurry coating plus pack cementation of Al	1338 K Good Erosion resistance
		PS 138	Platinum modified Al_2O_3 dispersed aluminide coating; Electrodeposition of Pt+ Al_2O_3 slurry coating + pack cementation of Al	1372 K Good hot corrosion oxidation resistance
		RS 138	Rhodium modified Al_2O_3 dispersed aluminide coating	1372 K "
		PR 138	Platinum-Rhodium modified Al_2O_3 dispersed aluminide coating	1372 K "
		TMT 1929	Silicon modified aluminide coating	1273 K
		TMT 1023	Cr-Si modified aluminide coating	1273 K
		TMT 213	Chromium rich aluminide coating	1273 K

Table V (cont'd)

Vendor	Source	Coating	Type and Process	Use or application
TMT	Calgary		EC 114 coating with variable NiAl composition	Diffusion aluminide Increased ductility
Sermatech	Dorval	SermalloyJ	Silicon modified aluminide coating: Al-Si slurry coating + pack cementation of Al	1477 K Claimed by vendor to have a low DBTT
Walbar	Oakville	Codep B$_1$	Diffusion aluminide coating	Oxidation
Vac-Aero	Oakville	Overlay coatings	Plasma Spray MCrAlY type	Oxidation and hot corrosion

Table VI

Commercial Hot Section Coatings available in the U.S.A.

Vendor	Source	Coating	Type and Process	Use or application
Union Carbide	Indianapolis	L-103 LCO-17 LCO-19	Cobalt alloy Cermet by (Cobalt alloy + Cr_2O_3) Detonation gun spray	811 K-1366 K Wear and Oxidation
		LCO-17A LCO-19A	Cobalt alloy + Al_2O_3 Detonation gun spray	"
		LCO-22 LCO-29 LCO-40	MCrAlY type overlay coating	Oxidation/ Sulfidation resistance
		LTB-8 LTB-12 LTB-13	Duplex Coating MCrAlY alloy undercoat plus partially stabilized zirconia outer coat	Thermal barrier plus oxidation and sulfidation
Allison	Indianapolis	AEP 100	Cr-Al Electrophoretic coating	Sulfidation
Airco Temescal	Berkeley, California	ATD-1	Electron beam Evaporation of NiCrAlY coatings	Excellent in oxidizing and sulfidizing environment, good mechanical properties

Table VI (cont'd)

Vendor	Source	Coating	Type and Process	Use or application
		ATD-2 ATD-4	EB-PVD of CoCrAlY coatings	
Alloy Surfaces	Wilmington Delaware	HI-275	Gas phase diffusion aluminide coating	Internal and external coatings
		PWA 73	Single step vapour deposited-pack Al-Si coating	For oxidation, Erosion and thermal fatigue resistance
		HI-15	Single step vapour deposited Cr/Al diffusion coating	1023 K 1498°K High temperature oxidation and corrosion
Turbine Component Corporation (Coating Technology)	Branford Connecticut	C-23	Gas Phase diffusion of Chromium	Hot Corrosion resistance
		C-23/19	Diffusion Cr-Al coating (inward type) chromizing + aluminizing	Hot Corrosion/ Oxidation resistance
		C-30	Gas phase diffusion of Al(outward type)	Internal cooling channels also thermal fatigue resistance
		SS82A	Pt modified aluminide coating	Hot corrosion resistance

Table VI (Cont'd)

Vendor	Source	Coating	Type and Process	Use or application
TCC (Cont'd)		SS82B	Pt-Cr modified aluminide coating	"
		SS82C	Pt-Cr modified aluminide coating	For cobalt alloys
		AVCO M 3960	NiCrAlY overlay plasma spray coating	Oxidation/Hot corrosion resistance
		AVCO M 3966	Thermal Barrier Coatings $ZrO_2 \, Y_2O_3$	
		PWA 53-33	Thermal Barrier ZrO_2 Mgo	
Chromizingo Co.	Gardena, California	UC	Gaseous diffusion coating of Al/cr	Hot corrosion resistance
		AL-14	Gaseous diffusion of Al, Si	"
		BB	Precious Metal + diffusion aluminizing	Oxidation/ Hot corrosion resistance
HITEMCO	Old Bethpage New York	NC 101	Pack diffusion aluminide	

Table VI (Cont'd)

Vendor	Source	Coating	Type and Process	Use or application
		SC 788	Overlay TBC ZrO$_2$ – Y$_2$O$_3$	
		SC 710	Overlay TBC Al$_2$O$_3$	
Chromalloy R & T	Orangeburg New York	RT 5	Chromium diffusion + Al diffusion in a pack	
		RT 11	Pack cementation of aluminide coatings	
		RT 17	Cr diffusion + Al diffusion	
		RT 19	Al pack diffusion	
		RT 21	Pack diffusion of Al (Inward type)	
		RT 22	Platinum deposition (electrolytic) + diffusion aluminizing	Oxidation/ Hot corrosion
		RT 30/34	Electron Beam PVD of CoCrAl Y coating	
		RT 44	Pt + Rh deposition (Electrolytic) + diffusion aluminizing	Oxidation/ Hot corrosion
		RT69	Gas Phase Al diffusion	Internal cooling passages

Table VI (cont'd)

Vendor	Source	Coating	Type and Process	Use or application
Howmet	Whitehall Michigan	MDC-1	Oxide dispersion aluminide coating	Oxidation/ sulfidation
		MDC-9	Duplex process chromizing + Aluminizing	"
		PWA-73	Al-Si pack diffusion coating	"
		PWA-273	PWA-73 followed by a second aluminizing	"
		PWA-252	Cr-Al pack diffusion coating	For cobalt alloys
		BC-22 BC-23	Hafnium and Platinum modified aluminide coatings	Oxidation/ sulfidation resistant
		LDC-2E PWA-36095	Platinum modified aluminide coatings	"
		PX-100	Vacuum plasma spray of MCrAlY overlay coatings	"
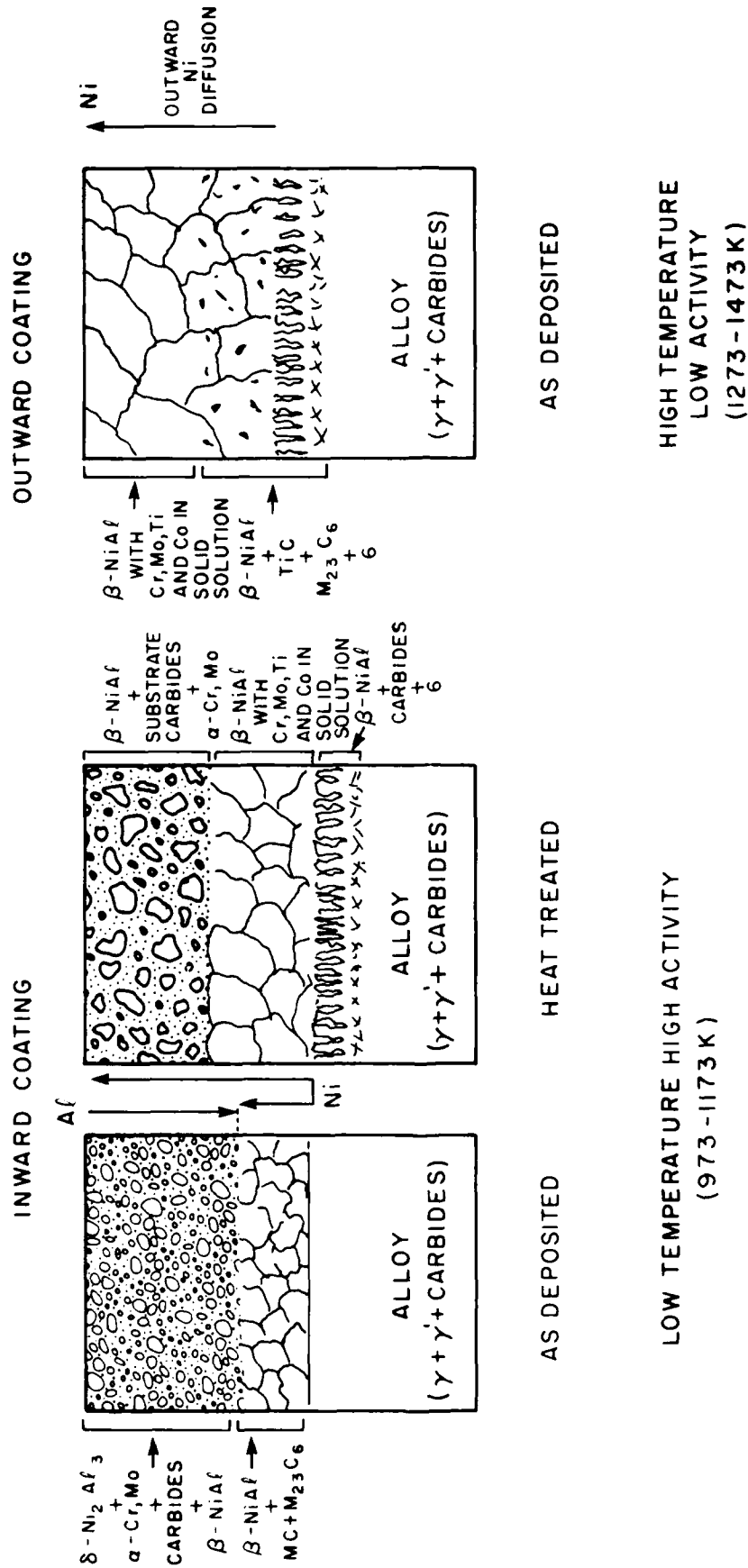
FIG. 1: SCHEMATIC REPRESENTATION OF THE MOCROSTRUCTURE, CONSTITUTION AND FORMATION MECHANISM OF ALUMINIDE COATINGS ON NICKEL BASED SUPERALLOYS
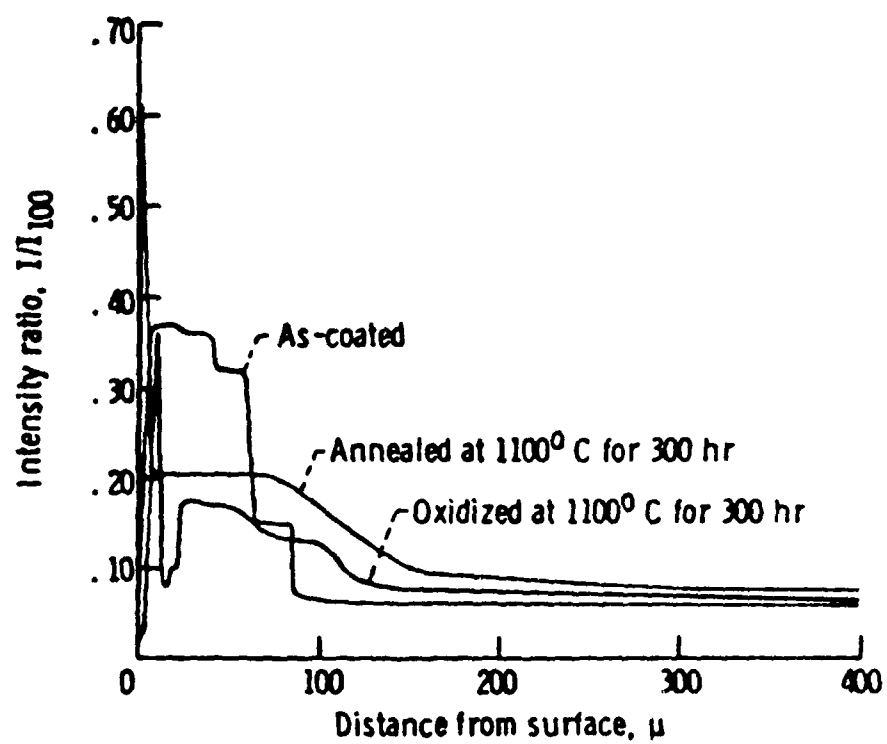
FIG. 2: ALUMINUM MICROPROBE PROFILES FOR PACK ALUMINIZED IN 100 (REF. 23)
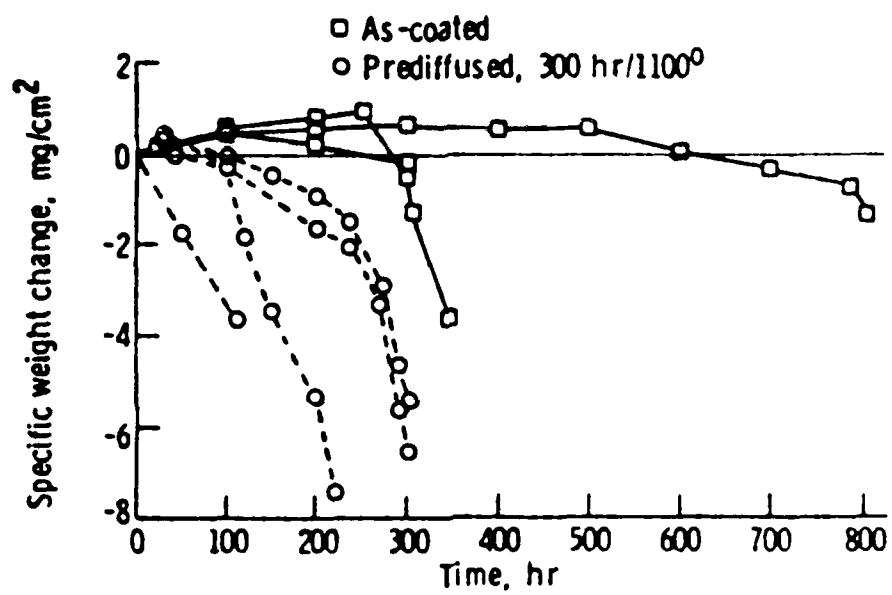
FIG. 3: ALUMINUM MICROPROBE PROFILES FOR PACK ALUMINIZED
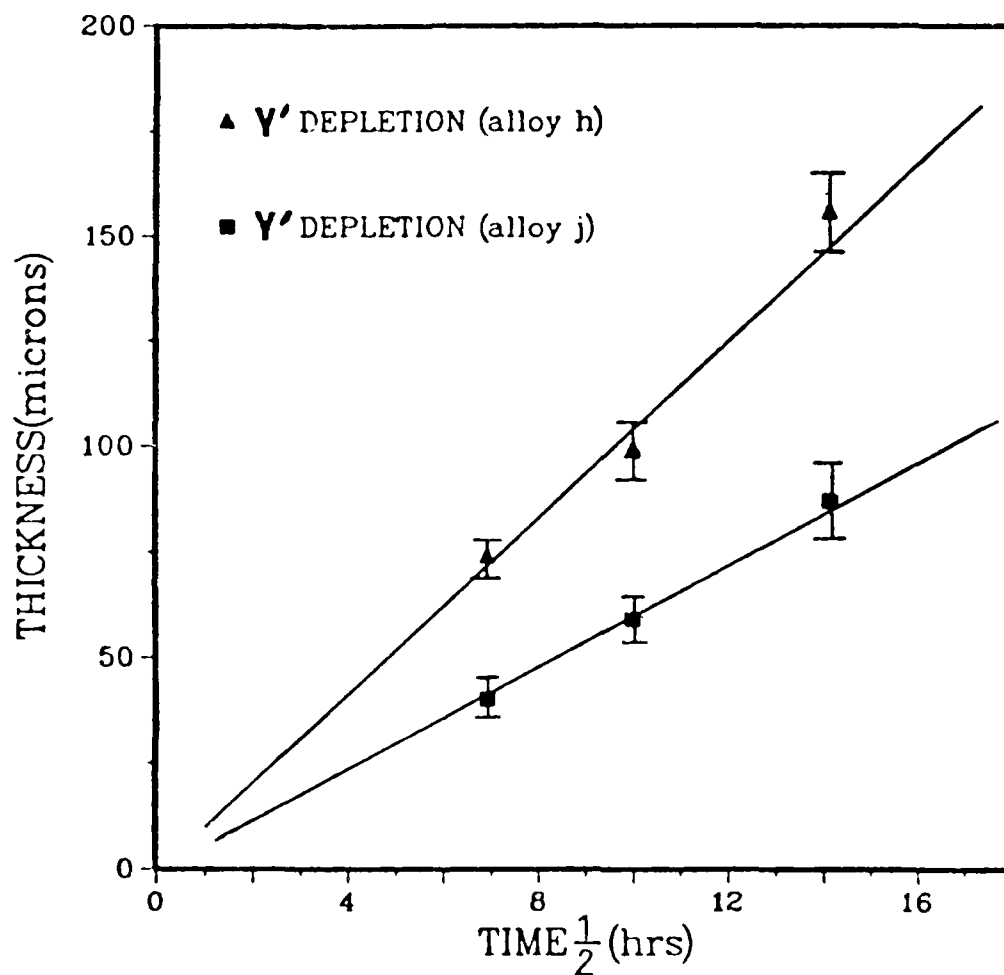IN 100 (1373K, IN 1h CYCLE FURNACE TESTS) (REF. 23)

FIG. 4: PARABOLIC THICKENING BEHAVIOUR OF SUBSTRATE DEPLETION
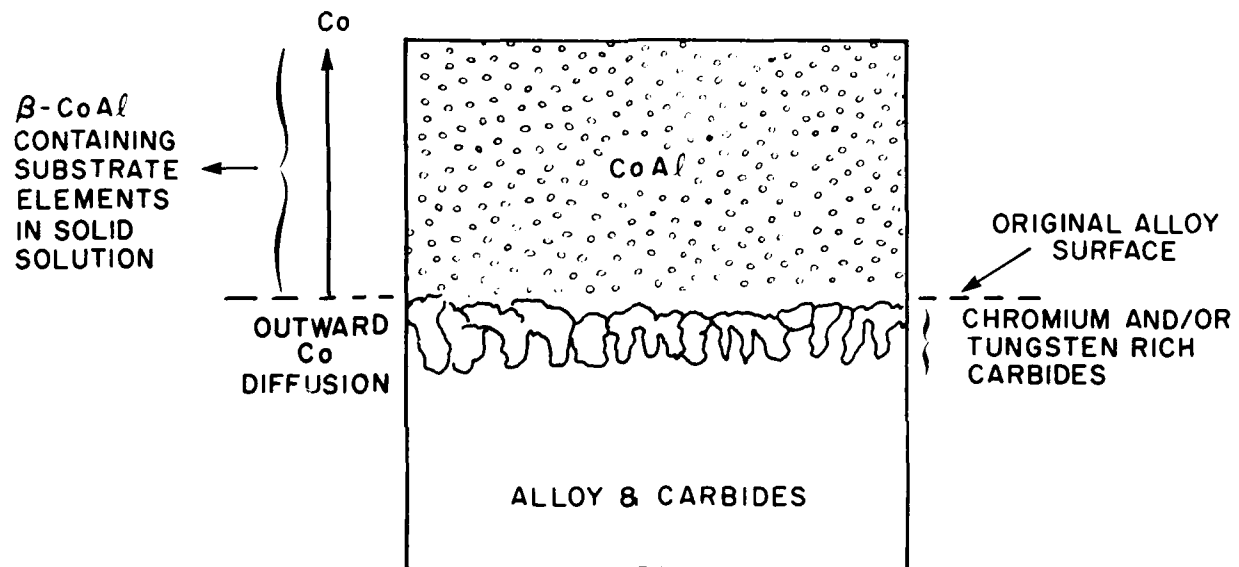ZONE THICKNESSES IN THE DIFFUSION COUPLES (REF. 34). ALLOY h
HAS NO TANTALUM WHEREAS ALLOY j CONTAINS 1 a/o TANTALUM

FIG. 5: LOW ACTIVITY ALUMINIDE COATING ON A COBALT
BASED SUPERALLOY
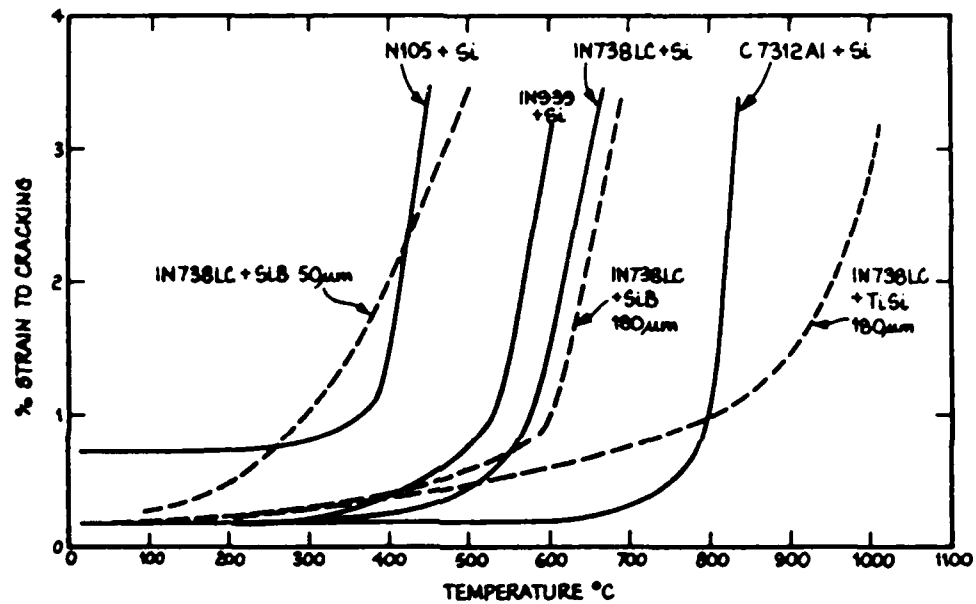
FIG. 6: THE EFFECTS OF SUBSTRATE COMPOSITION AND COATING THICKNESS
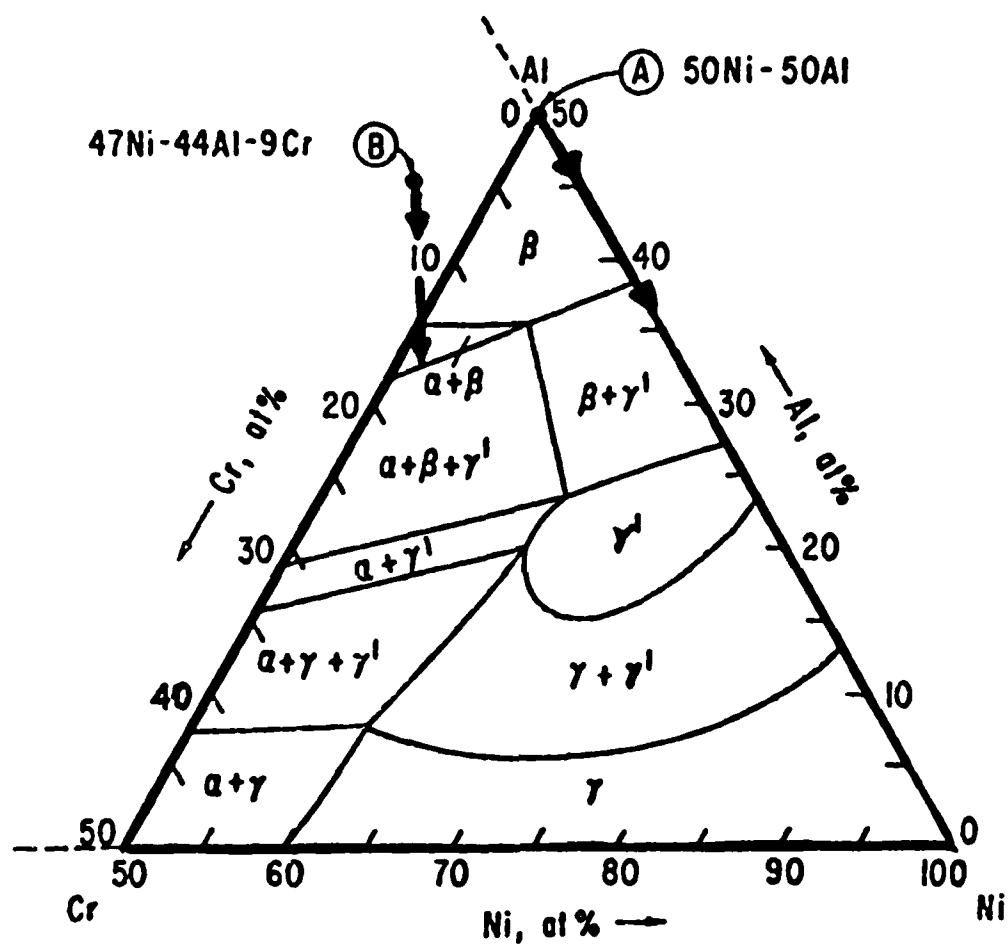ON THE DUCTILITY/TEMPERATURE CHARACTERISTICS OF SILICON
COATINGS (REFS. 43, 46)

FIG. 7: NICKEL RICH CORNER OF THE Ni-Al-Cr PHASE DIAGRAM AT
1123 K, AND THE IDEALIZED DEGRADATION PATHS FOR
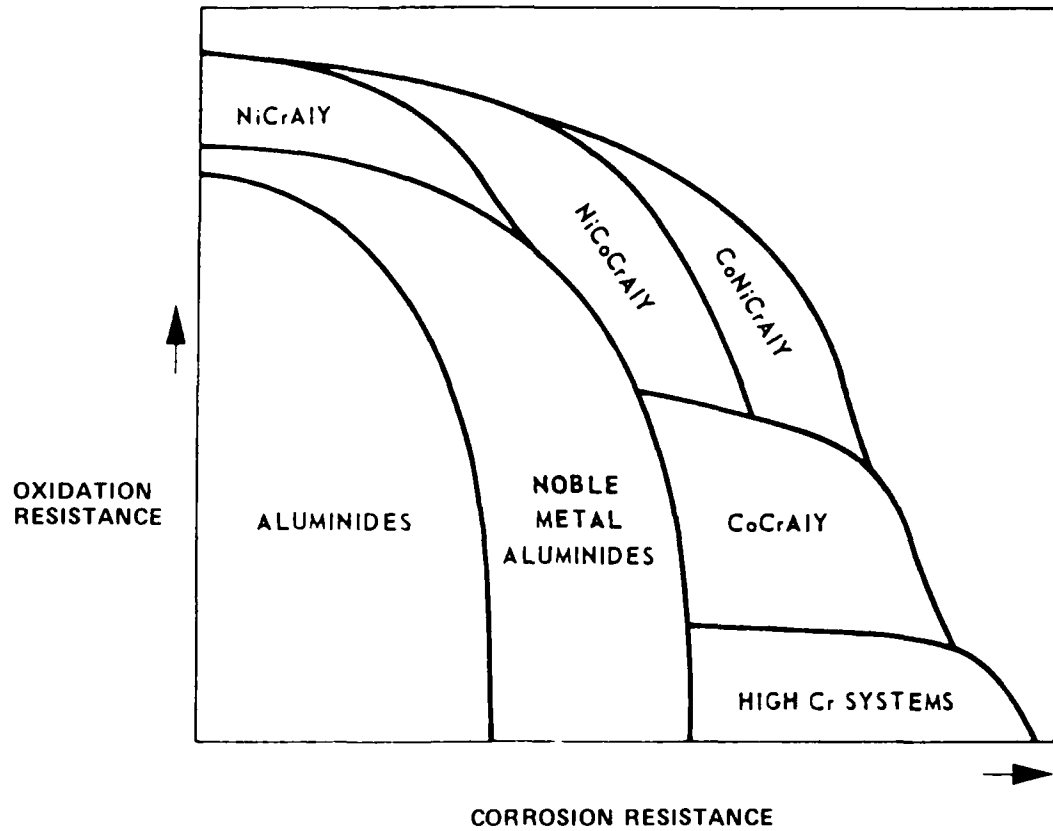a) NiAl (50:50) and b) NiAl + 10 a/o Cr (REF. 83)

FIG. 8: OXIDATION RESISTANCE VS. CORROSION RESISTANCE
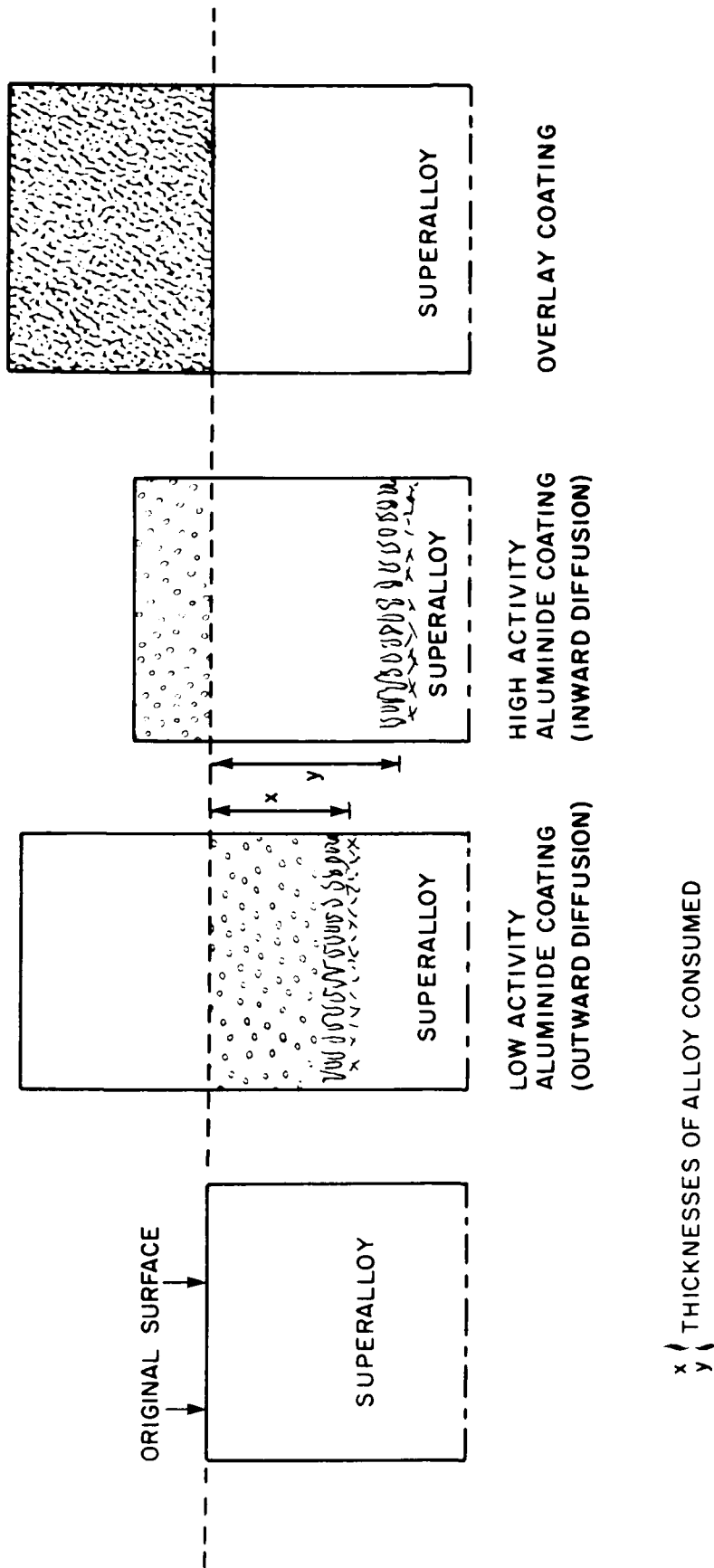FOR VARIOUS TYPES OF DIFFUSION AND
OVERLAY COATINGS (REF. 78)

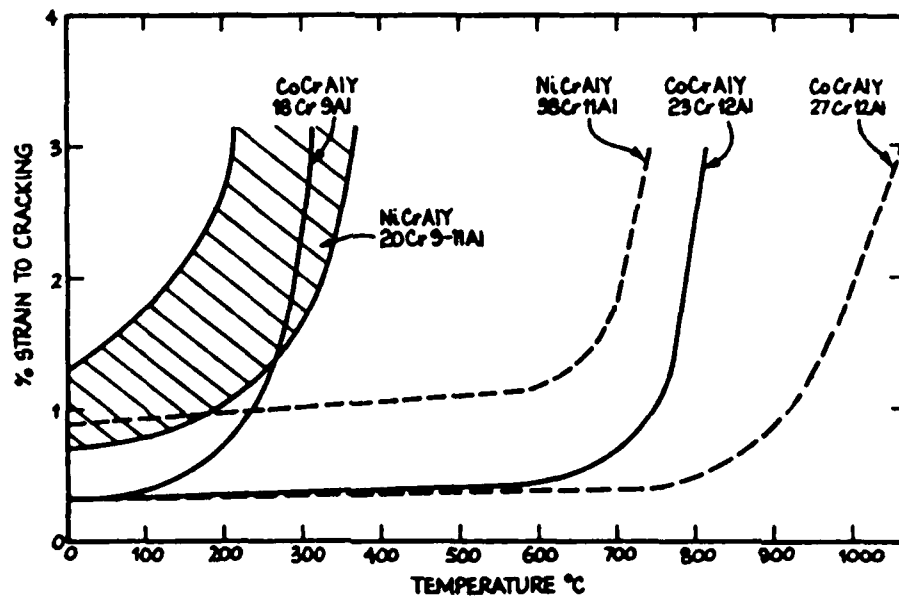FIG. 9: COMPARISON OF DIFFUSION AND OVERLAY COATINGS

FIG. 10: DUCTILITY/TEMPERATURE CHARACTERISTICS OF VARIOUS
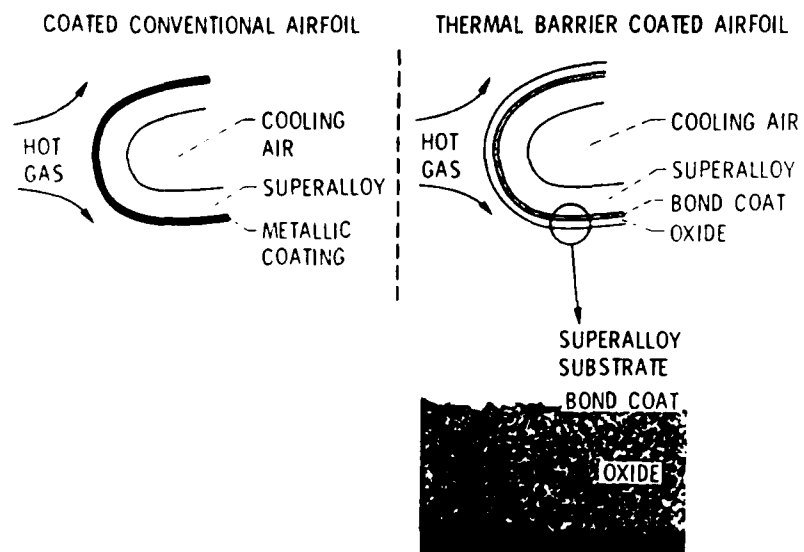MCrAlY TYPE OVERLAY COATINGS (REF. 42)

FIG. 11: A SCHEMATIC DRAWING OF THE THERMAL BARRIER COATING
(REF. 144)

REPORT DOCUMENTATION PAGE / PAGE DE DOCUMENTATION DE RAPPORT

REPORT/RAPPORT	REPORT/RAPPORT
NAE-AN-42	NRC No. 26475
1a	1b

REPORT SECURITY CLASSIFICATION CLASSIFICATION DE SÉCURITÉ DE RAPPORT	DISTRIBUTION (LIMITATIONS)
Unclassified	Unlimited
2	3

TITLE/SUBTITLE/TITRE/SOUS-TITRE
High Temperature Protective Coatings for Aero Engine Gas Turbine Components
4

AUTHOR(S)/AUTEUR(S)
P.C. Patnaik J.-P. Immarigeon
5

SERIES/SERIE
Aeronautical
6

CORPORATE AUTHOR/PERFORMING AGENCY/AUTEUR D'ENTREPRISE/AGENCE D'EXÉCUTION
National Research Council Canada   Structures and Materials Laboratory National Aeronautical Establishment
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9	10	11	12a	12b

NOTES
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DESCRIPTORS (KEY WORDS)/MOTS-CLÉS
1. Aircraft engines — coatings 2. Aircraft engines — temperature 3. Protective coatings. (Canada).
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SUMMARY/SOMMAIRE

Aluminide coatings have been widely used in the aircraft industries for the protection of gas turbine engine hot section components against oxidation and/or hot corrosion. This paper considers modes of coating degradation under conditions of cyclic oxidation, hot corrosion and corrosion-erosion interactions during service as well as the effects of interdiffusion between coating and substrate alloys either during service or coating application. It also discusses means of improving existing coatings as well as advanced coating systems currently under development. In assessing coating performance, consideration must be given to the influence coatings may have on substrate properties such as mechanical strength, resistance to creep and resistance to mechanical and thermal fatigue. Finally it is stressed that proven performance for a given coating/substrate combination is no guarantee that no deleterious reaction will occur, when the same coating is used with a different substrate alloy. Therefore, coating substitution requires requalification.

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END

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