RECENT APPROACHES TO THE DEVELOPMENT OF CORROSION RESISTANT COATINGS

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ABSTRACT

Two types of protective coatings are applied on the Ni or Co-base superalloys used in the high temperature - parts of aircraft or industrial turbines.

The coatings made of intermetallic compounds are mainly aluminides and sometimes silicides. They are most often produced by C.V.D. type techniques, especially pack-cementation. Their formation is generally governed by various diffusional mechanisms.

The overlay coatings are made of more or less complex alloys whose compositions depend on the projected applications (aircraft or industrial turbines). They are usually obtained by P.V.D. type techniques or by spraying.

These two types of coatings are presented in this paper with particular emphasis on the various possibilities to improve their properties. Different problems related to their deposition and use are discussed. Recent developments, such as thermal barriers are also included.

1. INTRODUCTION

Nickel or cobalt-base superalloys currently used in advanced gas

R. Brunetaud et al. (eds.), *High Temperature Alloys for Gas Turbines 1982*

turbines are almost always protected by coatings against oxidation and corrosion. Depending upon the temperature, three different corrosion mechanisms can be distinguished as shown in Figure 1 (1).

At relatively low temperature (about 700°C) acid fluxing sulphidation caused by a high SO_3 content in the combustion gas can occur ; at about 850 - 950°C, hot corrosion induced by molten sodium sulphate takes place whereas at higher temperature pure oxidation becomes more important.

Protective coatings for nickel or cobalt-base superalloys are either made of intermetallic compounds (aluminides, mainly, or silicides) or of complex alloys such as M, Cr, Al, Y alloys (M = Fe, Ni, Co).

Intermetallic compound coatings are generally obtained by C.V.D. type techniques and most often by pack-cementation ; their growth is governed by diffusion mechanisms. It results from the interaction between the substrate and the vapor phase which is rich in aluminum (or silicon) gaseous species.

Overlay coatings are obtained either by P.V.D. type techniques (thermal evaporation, sputtering) or by spraying (conventional plasma spraying at atmospheric pressure or low pressure plasma spraying).

However, other methods can be used to obtain these two types of coatings : for example, laser melting of a powdered alloy that can be either pre-deposited with a slurry or continously fed to the surface during the formation of the coating.

In this paper, recent developments are presented to show how the high temperature oxidation and corrosion resistance of these two types of protective coatings can be improved.

2. INTERMETALLIC COATINGS

They are most often aluminide coatings which can be used in the hottest parts of either aircraft engines or stationary turbines. The silicide type coatings, having a temperature limitation of 950°C, find their main application in industrial turbines. Nevertheless, they are also potentially attractive for the lower stages of aircraft turbines which are cooler.

2.1 Aluminide coatings

Aluminide coatings are of the NiAl type in the case of nickel-base superalloys (CoAl type for cobalt-base superalloys). These coatings are generally obtained by a very simple technique : pack cementation . Packs of very different compositions can be used. They mostly contain aluminum alloyed with other elements (chromium, titanium, nickel, silicon) which, among other things, lower the aluminum activity.

Depending upon this activity, two processes can be distinguished :

- the low activity process in which the NiAl (or CoAl) phase is directly produced by an outward diffusion of nickel (or cobalt)

- the high activity process in which a Ni_2Al_3 layer is first produced by an inward diffusion of aluminum ; a subsequent heat treatment, activating diffusion, then leads to the formation of NiAl.

The first process is carried out above 1000°C ; in the second one, the aluminizing treatment is performed at about 700°C while the temperature of the following diffusion treatment is generally higher than 1000°C.

These two processes lead to different coating morphologies :

- In the outer zone of the low activity coating, small amounts of elements from the base material are found. However, the composition of this zone also depends on the elements, other than aluminum, which are present in the pack (Figure 2).

- In the case of high activity coatings, the outer zone contains all the elements of the base material, either in solution or in the form of precipitates. These precipitates were either present in the original alloy (like carbides) or appeared during the coating formation (like Cr-rich precipitates), as shown in Figure 2.

However, it should be pointed out that, in both cases corresponding to the low and high activity processes, the composition of outer and inner zones is strongly dependant upon the chemical composition of the base material. Also, the conditions of the coating treatment, such as temperature and cooling rate, are unfortunately not always compatible with the heat treatment suitable for the base material. Moreover, with most pack cementation processes, it is not possible to get enough internal coatings of acceptable quality for cooled blades ; finally the masking problem is not easily solved.

So, several techniques have been developed to improve the aluminide coatings by changing their composition as shown in the following examples :

- co-deposition of elements from the pack
- pre-treating the superalloy (chromizing for example) prior to aluminizing
- deposition of a metal (like platinum) or an alloy on the superalloy prior to aluminizing.

In order to solve the problems stemming from the heat-treatment of the base material, the internal coating of cooled blades and the masking, the aluminizing process can be modified to either a high activity process or a vapor phase process.

The above examples are now described in more details.

2.1.1 Co-deposition of chromium and aluminum in one-step pack cementation process. In order to produce chromium-aluminum coatings in a single step pack process it is necessary to have a better understanding of the principles of the pack coat process, especially of aluminizing and chromizing. A mathematical model has therefore been developed for the deposition of aluminum on nickel base superalloys (2). The same model was used for chromizing and extended to the co-deposition of chromium and aluminum. So, after calculating the coating parameters, mixed chromium-aluminum coatings are produced.

More details are given in Appendix I.

2.1.2 Pre-treating prior to aluminizing. These pre-treatments are often a simple chromizing of the base material. They are used on high-strength low chromium content superalloys (Al_2O_3-fomer) in order to improve the corrosion resistance of the aluminide coatings.

Chromizing without the formation of an α-chromium layer

Numerous processes of graded chromizing have been studied since a few years (refer to Table I (3)) and some of them have even been recently industrially developed. Among these processes which correspond often to PWA 70 specifications, two of them can be detailed : the first one using the pack cementation technique and the second one being a vapor phase chromizing.

- HEURCHROME has thus developed a pack chromizing technique (HC 12) in which the pack contains (Cr, Ni, Al, NH_4Cl) powders.

The coating treatment is carried out at 1060°C for about 35 hours. By this process, the surface of the superalloy is enriched in chromium up to a thickness of about 20 µm. The resulting layer is in this case free of oxide and α-chromium (Figure 3).

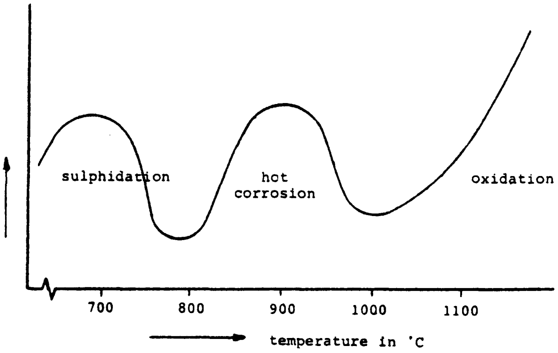
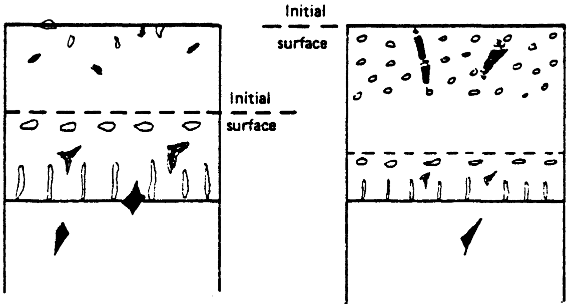


Fig. 1 — Possible corrosion mechanisms which can occur in a gas turbine as a function of temperature.



Low activity process (outward diffusion of Ni or Co)

High activity process (inward diffusion of Al)

Fig. 2 — Comparison of the structures of two Ni-Al-type coatings.

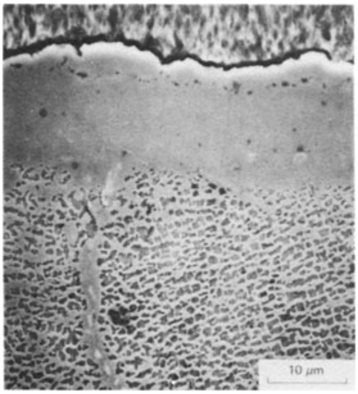


Fig. 3 — SEM micrograph of the HC 12 coating (PWA 70 specifications) on B 1900 superalloy.

TABLE I

2.1.2.a GRADED CHROMIZING

COATING	MANUFACTURER	SPECIFICATIONS	PROCEDURE
C1A (duplex)	SNECMA		2 steps - Cr diff. (vapor phase) + Al diff. (vapor phase) - 3h 1150°C
HC12	HEURCHROME	PWA70	1 step - Cr diff. (pack) - 35h 1060°C
HI24	ALLOY SURFACES	PWA70	1 step - Cr diff. (vapor phase) - 1060°C
MDC 3	HOWMET		1 step - Cr diff. (vapor phsae)
MDC3V	HOWMET	PWA70	1 step - Cr diff. (pack)
MERLP 19	CABOT	PWA70	1 step - Cr diff. (vapor phase) - 1060°C
PWA 70	PWA		1 step - Cr diff. (pack) - 1060°C
RT5 A_1	CHROMALLOY	PWA 70	1 step - Cr diff.
RT5 (duplex)	CHROMALLOY		2 steps - Cr diff. + Al diff. (pack)
Sylcralisation (duplex)	ONERA		2 steps - Cr diff. (pack) + Al diff. (pack) - 1050°C

2.1.2.b CHROMIZING WITH α-CHROMIUM FORMATION

COATING	MANUFACTURER	SPECIFICATIONS	PROCEDURE
DP 24	TEW		1 step - Cr diff. (pack)
ELCOAT 240	ELBAR		1 step - Cr diff. (pack) - 24h 1120°C
ELCOAT 37 (duplex)	ELBAR		2 steps - ELCOAT 240 + Al diff. (pack) 3h 950 - 1070°C
HI 32 (duplex)	ALLOY SURFACES	PWA 62	2 steps - Cr diff. (pack) + Al diff. (pack) 1050 - 1060°C
Inchromating	BBC		2 steps - Cr (electrodeposited) + diff. 2h 1100°C
PWA 62 (duplex)	PWA		2 steps - Cr diff. + Al diff. (pack)
RT17 (duplex)	CHROMALLOY	PWA 62	2 steps - Cr diff. + Al diff. (pack)

- SNECMA obtains similar results with a vapor phase process in which granules of chromium and ammonium chloride are used. The coating treatment is carried out at 1150°C for 3 hours. This pre-treatment, followed by the SNECMA vapor phase aluminizing, is called C1A. These two steps are shown in Figures 4a and 4b.

Other examples of vapor phase graded chromizing performed at lower temperature (about 1060°C) are given in Table I (3,4).

An older chromizing, interesting since it is associated with a tantalum enrichment of the alloy surface (co-deposition of Cr and Ta), can also be reported (ONERA process called "Tantalisation" (5)). However, its high cost has been detrimental to its industrial development even though the results obtained by coating alloys such as B 1900 or IN 100 were promising. The co-deposition of chromium and zirconium has also been produced in a similar way.

Chromizing with the formation of an α-chromium layer

ELBAR has recently developed on an industrial scale a chromizing pre-treatment leading to the formation of an α-chromium external scale 20 µm thick. This scale contains Al_2O_3 inclusions coming from the pack. Moreover, an internal chromium enriched diffusion zone about 30 µm thick has been observed. This process, followed by a high activity aluminizing, is called ELCOAT 37. The morphology of the coating thus obtained is shown in Figure 5. The outer zone is mainly made of α-chromium with NiAl precipitates, the intermediate zone of NiAl with α-chromium precipitates. Lastly, the inner diffusion zone contains more chromium than that of a simple aluminide coating.

Finally other processes using pack chromizing techniques are also reported in Table I (3, 4).

2.1.3 Pre-deposition prior to aluminizing. Pure metals (Pt, Rh, ...) or nickel or cobalt-base alloys can be pre-deposited.

Precious metal pre-deposits

The first process (LDC2) was developed by TEW : a Pt - layer 6 to 8 µm thick is electrodeposited prior to a high activity aluminizing at about 1050°C (6). The coating thus obtained has a thickness of 70 to 80 µm and presents an outer layer of $PtAl_2$; the major part of the coating consists of NiAl.

CHROMALLOY applies this process under TEW licence in a slightly modified way called RT22. The deposited Pt-layer is somewhat thinner than in the LDC2 process (5 to 7% of the entire coating thickness compared to 10% in the case of LDC2). This leads to a more ductile coating. Pre-deposits of rhodium and then of platinum have also been studied by CHROMALLOY (7). The aluminizing is then carried out in order to obtain a Pt rich outer layer similar to that obtained with the RT22 process and a Rh rich inner layer adjacent to the base material, the intermediate layer consisting of NiAl.

This type of coating (pre-deposit of precious metals followed by aluminizing) greatly improves both the oxidation and corrosion behaviors compared to those of simple aluminide coatings. Thus, it appears to be interesting for industrial turbine applications.

Alloy pre-deposit

In the simple aluminizing process, elements from the base material are included in the protective layer. Some of them, such as Mo, W and Ti sometimes decrease the protective properties of the coating. Alloy pre-deposits can help solve this problem. For example, experimental coatings made of a sputtered layer of Ni, Co, Cr, Al which is then aluminized exhibit a better oxidation and corrosion behavior than that of a simple aluminide (8).

Pre-deposits of more complex alloys*, produced most often by plasma spraying subsequently aluminized by a vapor phase process are now being studied by SNECMA with the aim of developing an industrial coating (C3A process) (9). The alloy pre-deposit and the final coating are respectively shown in Figures 6a and 6b. This coating presents some attractive features : near theoretical density, good adherence and very good corrosion resistance in the burner rig test. The high temperature oxidation resistance and interdiffusion between coating and base material are still to be evaluated. When the series of tests is completed, the pre-deposit composition will be optimized.

2.1.4 Compatibility between the coating and the superalloy heat treatment cycles. The effect of these thermal cycles is particularly important on certain nickel-base alloys whose creep strength is strongly dependent upon the γ' configuration.

Different thermal cycles are used for the high and low activity processes :

- in low activity pack-processes (outward diffusion of nickel) a single-step treatment is required i.e. 5 to 20 hours in the temperature range 1000 - 1100°C The cooling rates are slow due to the poor thermal conductivity of powder packs.

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*S67 developed by CRM : 22 wt%Cr - 10wt%Ni - 9,5wt%Ta - 12wt%Al - 0,5wt%Y - Co balance.

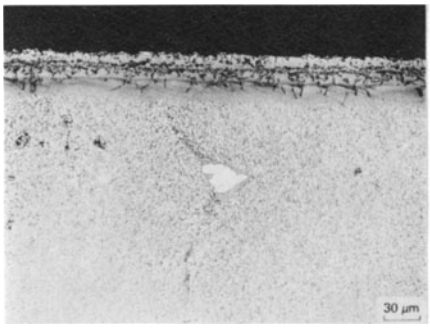

Fig. 4a — Optical micrograph of the C1A first step : vapor phase chromizing on IN 100 superalloy.

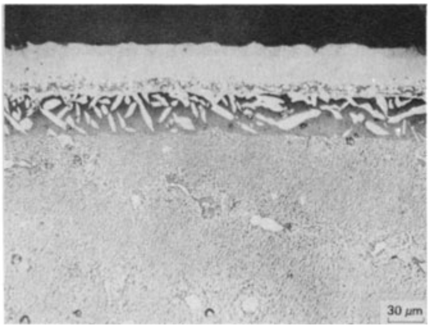

Fig. 4b — Optical micrograph of the C1A coating on IN 100 superalloy.

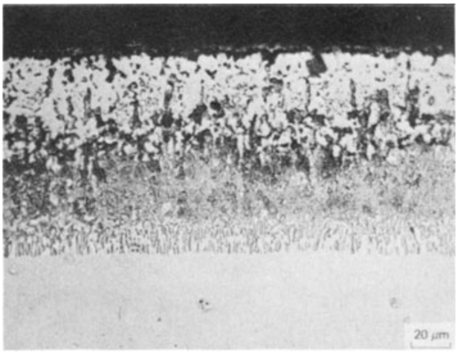

Fig. 5 — Optical micrograph of the ELCOAT 37 coating on IN 738 superalloy.

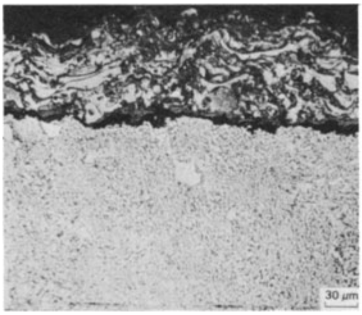

Fig. 6a — Optical micrograph of an atmospheric plasma sprayed S 67 coating on IN 100.

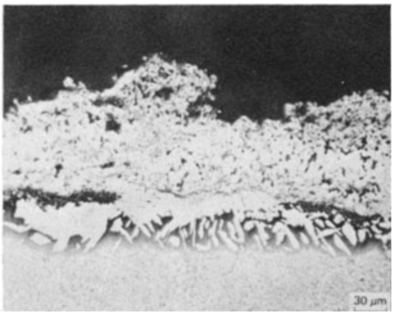

Fig. 6b — Optical micrograph of the C3A coating on IN 100 (without the required post-treatment).

2.1.5 Coatings for cooled blades. In general, the pack technique is not suitable for the protection of cooling channels especially those less than 0.5mm in diameter. This is due to the difficulties in feeding the reactants through the channels and in removing the pack mixture after the coating heat-treatment. Nevertheless, it must be pointed out that cooled blades protected by the pack cementation PWA 73 process are currently used in aircraft engines.

The vapor phase processes may offer a better solution for aluminizing cooling channels.

PWA has developed a process in which the substrate to be coated is isolated from the powder mixture. During the treatment the powder generates a metal carrying gaseous species within the coating chamber. These species then reach the substrate by gaseous diffusion. The characteristic of the gaseous transport agent required by this type of process is called "throwing power" (10). It is related to the ability to deposit on internal surfaces aluminum which interacts with the base material to form the internal aluminide coating. Various transport agents have been evaluated and their relative deposition rate measured. It was found that complex halides of aluminum and alkali metals have sufficient throwing power (sodium - aluminum fluoride, for instance) (10).

A novel approach to the problem of simultaneously metallizing the internal and external surfaces of turbine blades has been made by National Gas Turbine Establishment (NGTE) and Fulmer Research Institute (FRI) (11) (12). In this technique the components to be coated are placed in a retort separate from a near-conventional coating pack which consists of an aluminum source, a halide activator and an inert diluent. The retort is heated to 850°C and the pressure is then cycled by evacuating and re-filling with argon. Pressure cycle frequency may be in the range up to about ten times per minute. A pilot plant has been constructed and has demonstrated the capability of coating up to one thousand turbine blades simultaneously regardless of the complexity of the cooling channel configuration. Typically, the coatings on the external surface of a blade aerofoil are approximately 50 µm thick while the internal surface coatings are thinner (25µm) ; this minimizes the danger of blocking the narrower channels. The effect of the pressure pulse is to improve the transport of the reactant gases in and out of the cooling passages, to permit simultaneous coating of the internal and external surfaces of the blades. The process parameters are controlled to ensure that all of the reactants and by-products are gaseous so that no solid residues are formed inside the cooling channels. Also, since there is no direct contact between the blades and the aluminum source the aluminide coatings are

- in high activity techniques (inward diffusion of aluminum) two thermal cycles are usually required :
. a few hours in the temperature range 700-950°C for the pack aluminizing treatment ; the cooling rate is once again low ;
. a few hours at approximately 1150°C for the diffusion treatment ; in this case an appropriate cooling rate can be chosen.

The typical heat treatments for restoring the creep strength consist of a two-step treatment :
- dissolving the γ' precipitates (a few hours between 1080 and 1200°C). The cooling rate should be fast enough to avoid an unsatisfactory γ' precipitation.

- about 20 hours of heat treatment for a homogeneous γ' precipitation, around 850°C.

The dissolving treatment and the diffusion treatment in the case of high activity processes can be carried out together.

The single thermal cycle in the low activity pack-processes does not permit rapid cooling. Therefore the heat treatments required to restore the creep properties have to be performed on the coated alloy. However, the protective capability of the coating may be degraded. If the γ' dissolving heat treatment can be carried out below 1150°C, the coating will not endure important damage (for example, superalloys such as MARM 200, IN738 LC, UDIMET 500 and so on). On the other hand, if the γ' dissolving treatment must be carried out above 1200°C, the protective qualities of the coating may be degraded (for example, alloys such as COTAC, single crystals).

In conclusion, in the case of pack processes, the high activity aluminizing techniques are better suited for those nickel-base alloys whose creep rupture strength is sensitive to heat treatment.

The procedure for the different SNECMA vapor phase processes (cf §2.1.2) allows the heat-treatment cycle of the base material to be included in the coating cycle. Thus, in these processes, granules of chromium or chromium-aluminum alloys are used as metallic sources. They are held in perforated containers which prevent contact between them and the components to protect. The temperature of the coating treatment cycle can be increased to about 1150°C and is therefore compatible with the γ' dissolving treatment of most classical superalloys. In this case, the sintering of the powder pack is prevented by the use of granules. Moreover, the thermal mass of the system is low enough that sufficiently high cooling rates can be attained.

very uniform and free from contamination. On an experimental scale, the pressure pulse process has been adapted for coatings more advanced than plain aluminides. Some effort has been devoted to diffusion-type coatings rich in chromium and/or silicon. The method has been shown to be suitable for the generation of graded composition coatings whereby the final stage in the coating operation may include pulse aluminizing, chromizing or siliconizing to seal microcracks or other defects in the surfaces of overlay coatings deposited by plasma-spray or other methods (13) (cf § 3.3.1).

Karlsruhe University has developed a C.V.D. process based either on the reduction of $AlCl_3$ (or $AlBr_3$) by hydrogen or on the decomposition of preformed aluminum subchloride on the substrate (14). It has been shown that as far as the reduction of $AlCl_3$ (or $AlBr_3$) is concerned, coatings of suitable thicknesses could only be obtained above 1000°C ; on the other hand, if the preformed subchlorides are decomposed on the substrate, the coating operation can be performed at lower temperatures. The coating formed by this process is made of $Ni_2\ Al_3$ or NiAl and a diffusion heat-treatment is then performed to obtain the final aluminide coating.

The coating of cooled blades has also been extensively investigated by G.E.. Aluminide coatings were first obtained from an aluminum deposit resulting from the thermal decomposition of a metalorganic liquid (triisobutylaluminum - TIBA) at about 200°C (15). The aluminum deposit was then produced either by dipping the pieces into the liquid or by circulating the liquid throughout the blades. A heat-treatment of a few hours at 1050°C was then carried out in order to form a β-NiAl aluminide coating. It is worthwile to mention that other metallic deposits have also been produced : nickel from nickel carbonyl at 150 to 250°C and chromium from liquid dicumenylchromium at 350 to 450°C. The deposition of successive layers of Ni, Cr, Al then allows the formation of alloy coatings. More successful methods were then developed to coat internal surfaces : electroless deposition of nickel, slurry with a halide activator for chromium and aluminum deposition (16).

2.1.6 Masking problems. Masking is much easier when the aluminizing treatment is performed at a relatively low temperature (high activity processes). This simply consists of depositing a refractory powder slurry (i.e. ZrO_2) on areas where masking is required. However, one disadvantage of masking is that the powder pack could be polluted from the partial spalling of the mask while the components are being withdrawn from the pack.

It is more difficult to mask the components during low activity pack processes. Due to the rather high temperature required during these processes, the refractory powder slurry could interact with the pack and the superalloy and hence the mask would not suffice to prevent the formation of an aluminide coating. However, masking can be achieved by using a neutral alloy powder mixture tailored to the composition of each superalloy. The masking procedures may differ depending upon the shape of the component :

- ALLOY SURFACES' process is based on the building up of successive coatings by dipping to obtain a protective shell. The first slurry layers are made of a mixture which is neutral with respect to the composition of the superalloy. The last layers are made of almost pure chromium which becomes, after sintering, the mechanically resistant part of the shell.
- The method used by HEURCHROME consists of placing the blade root attachments in a can filled with the appropriate masking powder. This set-up is then placed in the pack powder for the aluminizing treatment.

Masking is much more easily achieved in the case of vapor phase processes such as SNECMA's C1A or C3A since it only requires the covering of the areas to be masked with a metallic sheet.

2.2 Silicide coatings

When deposited upon iron, nickel or cobalt-base alloys, simple silicides produced by a pack-technique exhibit very high oxidation and corrosion resistances, even in the presence of vanadium. However, it must be pointed out that these silicides have some drawbacks making them less useful in gas turbine coating applications.

First of all, they have a low melting point since NiSi can form a eutectic with Ni_2Si or $NiSi_2$ with a melting point of 965°C.

Secondly, these silicides are very brittle and lack resistance to thermal shock.

Lastly the diffusion of silicon from a surface silicide into an underlying superalloy at normal operating temperatures is not negligeable. This increase in silicon content of the superalloy can affect the mechanical properties of the base material.

For these reasons, only modified silicides can be used for turbine purposes.

At the University of Karlsruhe, work is being done on a laboratory scale on a mixed silicide coating produced by reaction sintering (17). Powders of nickel, chromium and a refractory metal (generally tantalum) of plasma spray quality are deposited by the slurry technique. Reaction sintering is carried out at 1000-1100°C in a 10^{-2} Pa vacuum. The coating consists of a γ - solid solution matrix of $Ni_6Cr_2Si_2$ composition and precipitates of Ni_2Ta_3Si. The oxidation and hot-corrosion behaviors of this type of coating are promising.

Another approach, the titanium silicide coating, was developed on a laboratory scale by Van Amerongen (18,19) at TNO during the first round of COST 50. ELBAR has developed this coating on an industrial scale under the name of ELCOAT 360 (20). In this process, the titanium is first deposited by ion plating. The titanium is then diffused into the base material ; during this step a Ni_3Ti layer is formed at the surface. Then a pack siliconizing process is carried out. A very complex layer is formed with G-phase, τ_3-phase and Ni_5Si_3. Figure 7 shows a micrograph of this type of titanium - silicon coating, which combines the oxidation/corrosion resistance of a simple silicide with some ductility and less silicon interdiffusion.

Other silicide coatings ($CrSi_2$, $MoSi_2$, $NiSi_2$) have been investigated on an experimental scale by FIAT (21). They used the laser technique to melt powders of suitable composition deposited on the substrates. More details are given in section 3.4.

3. OVERLAY COATINGS

The overlay coatings were widely developed during the seventies. They are most often alloys of the Ni (Co, Fe), Cr, Al, Y type. Their chromium and aluminum contents depend on their potential applications and are generally limited to 20% and 12% respectively. Higher chromium (or aluminum) content leads to an improvement of the coating corrosion (or oxidation) resistance but increases the coating brittleness. More complex alloys are presently being studied : additions of Ta, Hf, Si to M, Cr, Al, Y (22). Similarly, CRM has developed hot-corrosion resistant alloys for overlay coating applications (refer to Appendix II).

3.1 Electron beam vapor deposition

Up to now, electron beam evaporation has proved to be the best technique for producing overlay coatings. Its development results from a joint effort between PWA and AIRCO TEMESCAL in the USA.

If the theoretical process appears simple, the practical applications are very complex. It is necessary to work in a vacuum of 10^{-2} to 10^{-4} Pa. A continuous ingot feeding is used to maintain the height and composition of the molten pool. When low vapor pressure elements, such as Ta, Y, are to be evaporated, the molten pool must be richer in these elements than the feed ingot (refer to Appendix II). At steady-state, the vapor cloud composition is identical to that of the feed ingot. The size and shape of the pool depend on the application and on the number of pieces to be coated. Today's coater power supplies range from 100 to 200 kW. Evaporation rates of 25 µm/min are currently obtained (23).

The deposit structure is generally columnar with open intergranular porosity which decreases the coating corrosion and oxidation performances. The coating behavior can be improved by different post-treatments : surface melting by laser or electron beam heating, shot-peening followed by an appropriate heat-treatment, superficial aluminizing of the deposit, graded aluminizing or chromizing to fill the porosity (pulse process) (11). Once the open porosity has been closed by means of shot-peening or superficial aluminizing, a hot isostatic pressing (HIP) treatment can be carried out to further densify the coating.

3.2 Sputtering

In contrast to the electron beam vapor deposition the sputtering technique had not been developed for overlay coating applications before the mid-seventies. This technique may offer some advantages when high melting metals or complex alloys are used as coating materials. In the case of complex alloy deposition, the coating composition can be easily controlled. One of the major drawbacks of this method has been the low deposition rate obtained with conventional diode or triode sputtering : 10% (or less) of that obtained with the thermal evaporation technique. The introduction of high-rate sputtering in the last few years has made possible the use of this technique for high temperature coating applications. In this case, the plasma is concentrated in front of the cathode by means of a magnetic field. Under these conditions, the deposition rate approaches that obtained with thermal evaporation.

Using a high-rate sputtering system (cathode magnetron), the CRM has deposited S57[*] and S77[*] on different superalloy substrates. As far as the deposit composition is concerned, the first results have shown no noticeable difference between the sputtered layer and the target.

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[*] S57 : 25wt%Cr - 10wt%Ni - 5wt%Ta - 3wt%Al - 0,5wt%Y - Co balance

[*] S77 : 25 wt%Cr - 10wr%Ni - 5wt%Ta - 7wt%Al - 0,5wt%Y - Co balance

S57 deposits on different alloys have also been made at ONERA using a modified triode system whereby deposition rates of about 10 µm/h could be attained (8). In some cases, the coatings contain less aluminum than the target. Additional studies are now in progress in order to clarify this point (24).

Figures 8a and 8b illustrate that a good compatibility between the coating and the substrate is required for the following reasons :

- high interdiffusion rates between cobalt-base coatings and nickel-base superalloy (Figure 8a) are not compatible with high temperature applications, especially in the case of the thin walls of the cooled blades.

- the carbide precipitation at the interface between the coating and the superalloy can induce spalling of the coating, particularly when the components are subjected to thermal cycling (Figure 8b).

Studies are now being conducted by PWA to apply the sputtering technique to the deposition of Ni, Co, Cr, Al, Y alloys. In this process, a thermoionic emitter (triode system) is used to increase the degree of ionization in the plasma (25).

The structure of the sputtered layer depends on the coating parameters, especially on the substrate temperature. In general, if the substrate is near room temperature, the deposit exhibits a microcrystalline structure with more or less columnar crystals hundreds to thousands Å in size. Between 0.5 and 0.8Tm (melting point of the coating material) the structure is columnar with coarse grains and equiaxe above. The density of the deposited material (metal or alloy) is very close to that of the corresponding base material. The coatings are free of porosity and it is not necessary to apply a post-treatment such as shot-peening, heat treatment, superficial aluminizing etc...

3.3 Plasma spraying

3.3.1 Atmospheric plasma spraying. Arc plasma spraying has been used for many years to coat components (or parts of components) to improve their resistance to wear, abrasion or thermal shock. The deposited materials can be metals, alloys, carbides or oxides.

These coatings improve the base material behavior. However, they have drawbacks (porosity, oxide inclusions, poor adherence) which limit their use and development, especially for high temperature applications. High temperature oxidation tests performed at PWA have shown that the lifetime of an atmospheric plasma sprayed M, Cr, Al, Y coating was about half that of the same M, Cr, Al, Y obtained by thermal evaporation (26).

Suitable post-treatments (cf §3.1) can be used to enhance the coating resistance to oxidation and corrosion. The following example shows the advantage of the pulse aluminizing treatment described in § 2.1.5. A microsection of a localized defective region of a blade which had been plasma-sprayed with a Co, Ni Cr, Al, Y coating subsequently heat-treated and peened is shown in Figure 9a. Figure 9b shows a typical microstructure of a plasma-sprayed Co, Ni, Cr, Al, Y coating on a blade surface which was subsequently pulse-aluminized and heat-treated to recover the creep-rupture properties of the substrate alloy. The pulse-aluminizing treatment seals surface-connected defects and modifies the surface composition of the original plasma sprayed coating. Results of laboratory tests and high velocity corrosion rig tests on various samples and turbine rotor blades protected by these graded composition coatings have been encouraging (27). These coatings have also behaved extremely well in thermal fatigue tests at NGTE (some of the results are included in another paper being presented at this conference) (28).

In the case of coatings made of simple alloys (Co-Cr based alloys for gas turbine applications), the oxidation of the sprayed powders may be reduced by the addition of silicon and boron. More adherent and less porous coatings are thus formed (refer to Appendix III).

3.3.2 Low pressure plasma spraying (LPPS). The various drawbacks of atmospheric plasma spraying can be eliminated by using a chamber under partial vacuum or reduced inert gas pressure. The low pressure allows very high particle and gas velocities (above Mach 3) to be attained. Combined with efficient particle heating, it produces high coating density and virtually no unmelted particles. The absence of oxides improves coating adherence and particle cohesion. The vacuum allows the use of the plasma gun to clean and heat the workpiece. Additional heating can be obtained by positively biasing the parts with respect to the gun (transferred arc).

The LPPS technique is likely to be cheaper than the EB vapor deposition as far as equipment and operating costs are concerned. The surface roughness of these deposits generally appears inacceptable. This roughness depends on both the chemical composition of the coating and on the particle size of the starting powder. Generally finishing techniques are used to diminish the surface roughness. It has also been observed that the LPPS M, Cr, Al, Y coatings are more ductile than the vapor deposited similar M, Cr, Al, Y (22). The post-treatments cited in § 3.1 can be applied to LPPS coatings. However, a simple vacuum heat-treatment is generally sufficient.

In the joint COST 50 action, studies on LPPS coatings have been carried out at MTU : deposition of Ni, Co, Cr, Al, Y alloys

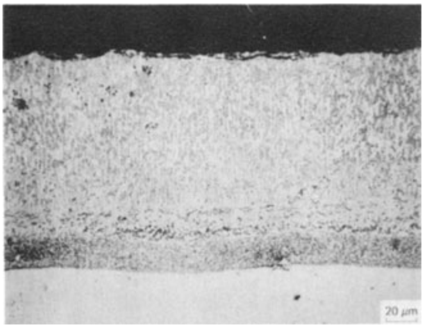


Fig. 7 — Optical micrograph of the ELCOAT 360 silicide coating.

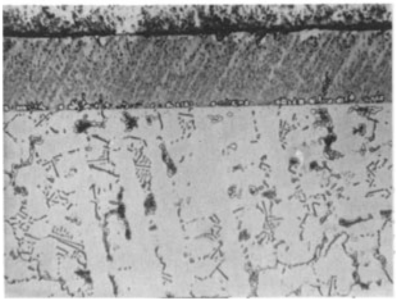


Fig. 8a — Optical micrograph of a 557 sputtered layer on COTAC 3 alloy after 400 h of isothermal oxidation at 1100°C.

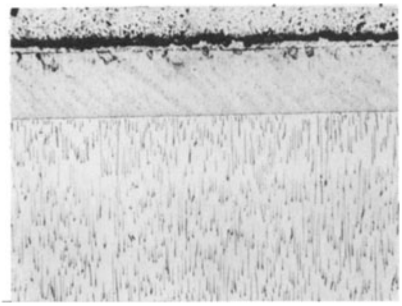


Fig. 8b — Optical micrograph of a 557 sputtered layer on MARM 509 alloy after 400 h of isothermal oxidation at 1100°C.

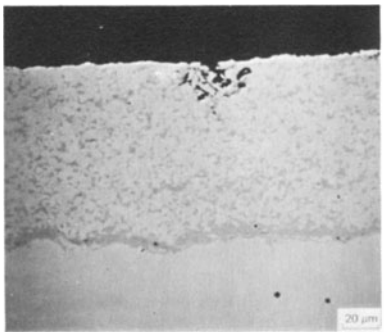


Fig. 9a — SEM micrograph of a plasma sprayed Co,Ni,Cr,Al,Y coating heat-treated and peened.

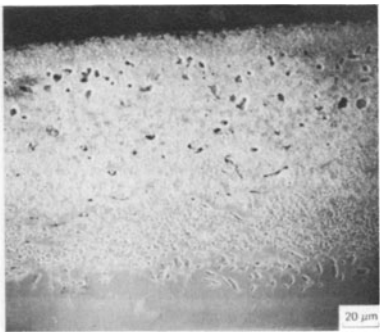


Fig. 9b — SEM micrograph of the same coating as (9a) subsequently pulse-aluminized.

(nickel-base or cobalt-base alloys with additions of tantalum) (29). The deposit structure of a Ni, Co, Cr, Al, Y, Ta LPPS coating is shown in Figure 10.

3.4 Other processes

3.4.1 Laser assisted techniques. The laser technique has been applied in the coating technology to melt superficially porous coatings in order to further densify them. For example, overlay coatings obtained by thermal evaporation or by atmospheric plasma spraying can thus be densified (cf §3.1). However, this technique when applied on atmospheric plasma sprayed Fe, Cr, Al, Y coatings did not give results as good as those obtained by electron beam melting (30).

In the joint action COST 50, FIAT has applied the laser technique to produce coatings (Cr, Ni-Cr-Al alloys, silicides of Cr, Mo, Ni) from different pre-deposits : electrolytical pre-deposits containing embedded powders, aluminum sheet cladding, powders deposited with a binder and pre-sintered (21). The major problems encountered were in the change in the surface roughness due to the surface melting, the selective evaporation of some of the coating elements, the cracking of the coating during cooling.

Studies (cited in (31)) are now being conducted with the aim of directly producing protective layers. In this process, still in the experimental stage, powder is fed from the side into a high-power laser beam and is melted in the beam.

3.4.2 Cladding. GE has evaluated diffusion bonded, corrosion resistant sheet cladding since 1970 as a potential means for protecting industrial gas turbine buckets during extended service in corrosive petroleum or coalfired environments. The principal cladding alloys investigated were GE 2541* and S57** (32). Metallographic evaluation of maximum penetration depth after the hot-corrosion tests indicated that pack aluminized S57 is superior to GE 2541 under all conditions of environment and temperature. These tests were performed on an INCO 738 substrate. Another important observation from these studies is the significantly higher rate of the Fe-Ni interdiffusion between GE 2541 and INCO 738 compared to the rate of Co-Ni interdiffusion between S57 and INCO 738.

GE 2541* : 25wt%Cr - 4wt%Al - 1wt%Y - Fe balance

S57** : 25wt%Cr - 3wt%Al - 10wt%Ni - 5wt.%Ta - 0,5wt%Y Co balance

4. THERMAL BARRIER COATINGS

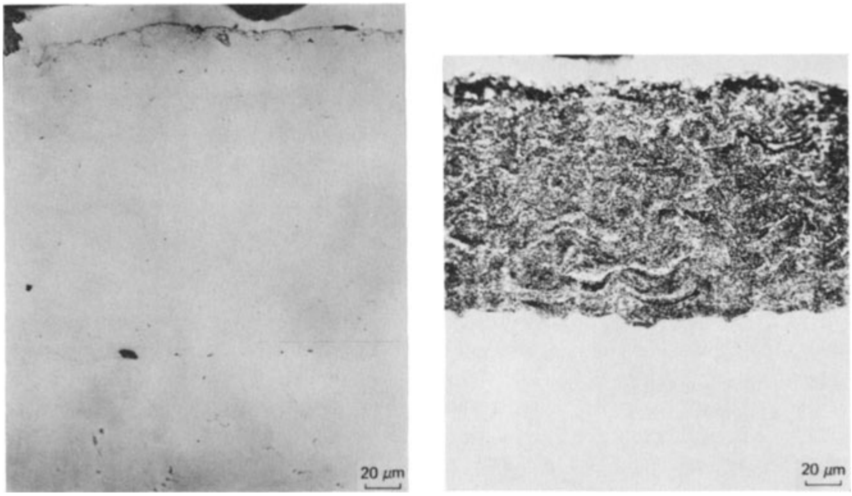
Thermal barrier coatings consist of materials of low thermal conductivity which therefore limit the heat flow through the surface. In the case of internally cooled blades or vanes the temperature of the base material is lowered, and as a result, lifetime is increased. This temperature drop in the base material can also be used to increase the gas temperature as well as the efficiency of the gas turbine. Another advantage of a thermal barrier coating is the temperature regulating effect. During the heat up period, the difference in temperature between thick and thin parts will be remarkably lowered using a thermal barrier coating. In this case the coating controls the heat flow. This also means that the problems arising with low cycle fatigue caused by thermal fatigue can be diminished by the use of thermal barrier coatings.

Materials considered as thermal barrier coatings are in general oxides and eventually carbides and nitrides. The important properties of the coating material can be divided in four groups : strength, thermal conductivity, stability, compatibility with the base material.

The strength of most of the thermal barrier materials is much less than that of a superalloy in the temperature range 700 to 1000°C. Another inherent drawback of most ceramics is their brittleness.

The thermal conductivity of zirconium oxide is several orders of magnitude lower than that of other ceramics. It is thus well suited for thermal barrier applications. Zirconia is monoclinic at room temperature and switches to a tetragonal form between 1000 and 1100°C with a large volume change (up to 7%) which is detrimental to the mechanical integrity of sintered shapes during cooling. Above 2370°C, ZrO_2 is cubic (33). Additions of 3 to 15% of calcium oxide, cerium oxide, yttrium oxide or magnesium oxide stabilize the cubic structure over the entire temperature range and therefore prevent the ceramic from microcracking during cooling. By varying the amount of oxide additions, randomly segmented or microcracked structure can be obtained (34).

The major factor limiting the thermal barrier compatibility with the substrate is the thermal expansion mismatch between the coating and the substrate. A M, Cr, Al, Y layer is generally used as a compliant bonding layer between the ceramic and the base material as well as an oxidation and corrosion resistant layer. The M, Cr, Al, Y and stabilized zirconia layers are most often deposited by plasma-spraying (Figure 11). In this case, thermal spalling induced by flaws in the coating limits the lifetime of ceramic barriers.



Unetched *Etched*

Fig. 10 – Optical micrograph of a Ni,Co,Cr,Al,Y,Ta coating deposited by LPPS.

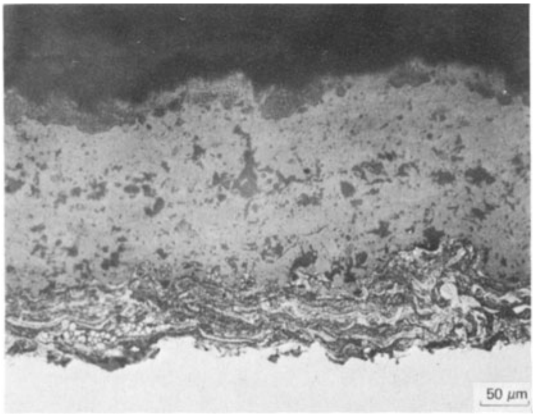


Fig. 11 – Plasma sprayed MgO stabilized ZrO_2 with a Co,Cr,Al,Y bond coat.

Different attempts have been made to increase the thermal barrier lifetime under repeated thermal shocks (34, 35) : use of porosity controlled, segmented or microcracked stabilized zirconia and control of the substrate temperature during coating formation.

The thermal barrier lifetime also depends on its corrosion resistance : the Y_2O_3 stabilized ZrO_2 shows a better corrosion resistance than the others. Compositional changes in the M, Cr, Al, Y bond and in the amount of Y_2O_3 can have a greater effect on the lifetime of the system than does the substrate expansion (36).

Most of the ceramic coatings are presently made by plasma spraying. Sputtering and thermal evaporation techniques are also being investigated (37, 23). The use of a graded compositional change between coating and ceramic (i.e. M, Cr, Al, Y - M, Cr, Al, Y enriched in ceramic - ceramic) seems attractive since it could be beneficial to stress accomodation. However, some difficulties are encountered for producing these mixed layers by the plasma spraying technique.

5. CONCLUSION

In aircraft engine applications, the aluminide coatings are still mostly used. Recently, different ways of improving their performance have been explored (co-deposition of Cr and Al, alloy predeposit, etc) and some new processes are now being developed.

As far as the overlay coatings are concerned (M, Cr, Al, Y alloy deposits with addition of Ta, Hf), some problems have not been yet fully solved : post-treatment, coating/substrate interdiffusion, stripping, cost etc. Among the available techiques for depositing alloy coatings, the Low Plasma Pressure Spraying Technique (LPPS), seems very promising and should be widely used to protect rather large size components. In the case of small blade (or vane) protection, the sputtering technique will probably be developed in contrast to the thermal evaporation technique. For aircraft engine lower stage applications, silicide coatings are now being evaluated.

In industrial turbine applications, silicides, modified aluminides (Pt pre-deposit, Cr enrichment) and chromium-rich overlay coatings are mainly used. In this case, less complex alloys are generally used as overlay coating materials compared to those currently used in aircraft engine applications.

ACKNOWLEDGMENTS

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APPENDIX I (from G. MARIJNISSEN)

Study of gas phase coating mechanisms (NL3)

1. A QUANTITATIVE MODEL FOR ALUMINIZING

During aluminizing the coating is obtained by treating the parts at a high temperature in a pack box, which contains a mixture of aluminum powder, an inert filler material and an activator (for instance 1-3 wt% NH_4CL, 1-15 wt% Al, balance Al_2O_3 (1) (2)). The coating obtained consists of a NiAl layer which forms an aluminum oxide scale on its surface during operation of the gas turbine, so providing protection for the part. In order to better understand the role of temperature and other parameters during the formation of the coating, this paper presents a mathematical model based, like the Gupta model (3), on thermodynamics and gaseous diffusion of the halide compounds on the one hand, and solid state diffusion on the other.

In the model described in this paper the steady state between the two types of diffusion, one transporting aluminum from the pack to the surface, the other transporting aluminum from the surface into the substrate material, gives the solution to the problem.

The model predicts : the growth rate of the coating as a function of temperature, and the phases formed on the surface and the composition of the coating as a function of temperature and aluminum content of the pack. These predictions agree very well with experiments on coatings formed on pure nickel and on B-1900 nickel-base alloy.

The model was developed for a coating pack with Al as the coating substance, NH_4Cl as the activator and an inert filler material.

We also used the same model with good results for chromizing, and the model is possibly useful for other pack coating processes.

2. THE CO-DEPOSITION OF TWO ELEMENTS

From calculations it is clear that the chromium depletion is much slower than the aluminum depletion.

The growth rates for chromium and aluminum as a function of temperature are given in Fig. I1a. This figure flows that the region where solid state diffusion for chromium is rate-controlling, lies at much higher temperature than that for aluminum.

Also the growth rate of the chromium layer, under normal circumstances in the region of 1000°C is orders of magnitude lower than that of the aluminum layers. By the choice of a special composition and the use of specific aluminum decelerating activators it is possible to obtain deposition rates for chromium and aluminum of the same order of magnitude at temperatures of about 1000°C. In this region (see Fig. I1b) gas diffusion is rate controlling for aluminum and solid state diffusion is rate controlling for chromium. This means that the deposition rate for chromium, is much more temperature dependent that the deposition rate for aluminum. The process therefore becomes very critical when a coating with a special chemical composition is to be obtained.

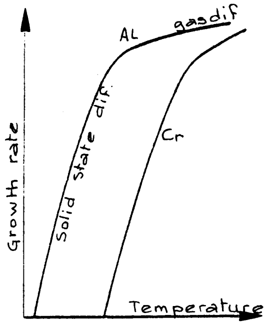

Fig. I-1a – Coating growth rate as a function of temperature.

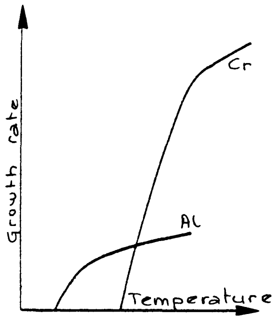

Fig. I-1b – Growth rate as a function of temperature with adjusted pack composition.

3. PRODUCTION OF MIXED COATINGS

Having calculated the parameters, a number of coating tests are done. Depending upon the pack composition, the nature of the activators, the amount of metallic parts and the use of alloyed or blended metals, the coating type and composition vary. The influence of temperature is very important.

Fig. I2 gives a photo micrograph of a mixed coating produced in a single step pack process and Fig. I3 shows its chemical composition. On the outside, the coating consists of an α-chromium layer. The medium part of the coating is of the NiAl type and the diffusion area on the base material is comparable with a normal aluminide coating with the difference that the chromium content is higher.

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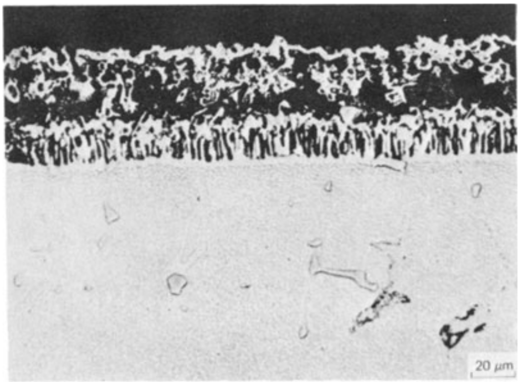
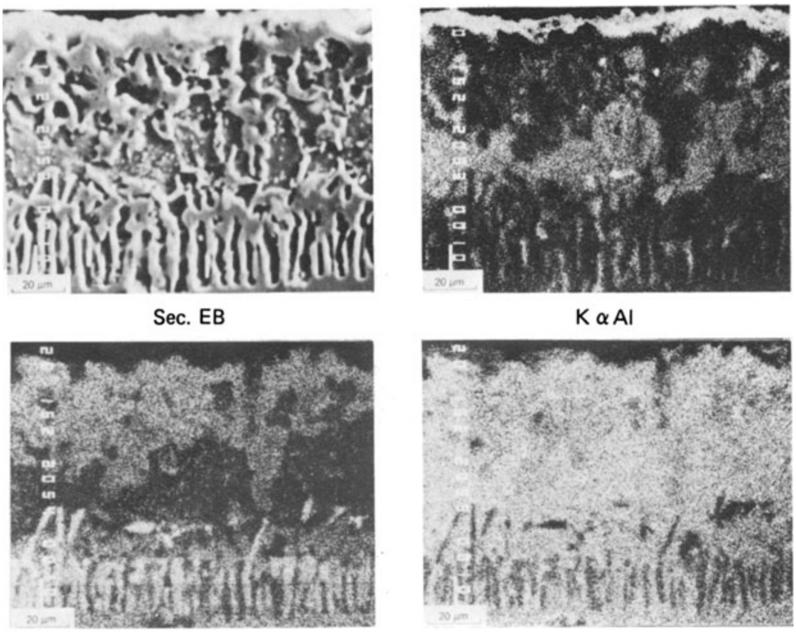


Fig. I-2 — Photo micrograph of a single step chromium aluminium coating. Magn : 500 x.



Sec. EB

K α Al

K α Ni

K α Cr

Fig. I-3 — Chromium aluminium coating on IN738.

APPENDIX II (from A. DAVIN)

Property evaluation of hot corrosion resistant coatings prepared by thermal evaporation (B1/1)

1. DEVELOPMENT OF Co-Cr-Ta-Al-Y-Ni alloys

Investigations have been conducted at CRM laboratories to develop a cobalt base superalloy with high mechanical characteristics and good oxidation and corrosion resistance. Studies of the oxidation resistance of Co-Cr alloys have shown that Cr, Ta, Al, Y contributed significantly to the oxidation, sulphidation and hot corrosion resistance of cobalt alloys (1).

The intrinsic corrosion resistance of an alloy containing 25Cr-10Ni- 5Ta-3Al and 0.5Y has been compared to other current cobalt base alloys. It appeared that this alloy (S 57) is far superior to other alloys even chromium-rich alloys (for example FS 414 con-n-taining about 30% chromium). Because of its excellent resistance in corrosive environments the application of S 57 as a protective coating appeared of particular interest.

2. OPTIMIZATION OF THE HOT CORROSION RESISTANT ALLOY S57

Protective coating applications, in particular for coatings produced by plasma spraying do not necessarily require powders of alloys of such high formability as S 57. Therefore an optimization of the S57 composition has been undertaken aiming at increasing further its hot corrosion resistance at the least expense of its formability.

Several cast experimental grades derived from the S57 composition by modifying the Ta and Al contents were prepared and tested under hot corrosion conditions. Some of the 10%Al alloys appeared very brittle and were heavily cracked during cooling after casting. The results have shown that the highest corrosion resistance was exhibited by the S67 grade containing Co-25Cr-10Al-10Ta-10Ni and 0.5Y. On the other hand, the tantalum free and aluminum free alloys exhibited the largest degrations.

It must be pointed out that the observed improvement of hot corrosion resistance over the basic S57 alloy was achieved at a large expense of the material ductility due to the increase in Al and Ta contents. This factor is to be kept in mind for coating applications even by plasma spraying, since the mechanical behaviour of the coating depends on the sprayed material ductility. Different alloy compositions between S57 and S67 have been defined and, among these compositions, the S77 alloy containing 5%Ta and 7%Al appears to present the best compromise between ductility and hot corrosion resistance.

3. PREPARATION OF COATINGS BY THERMAL EVAPORATION

The coatings have been produced in a Leybold Heraeus chamber (height 700 mm-diameter 700 mm) equipped with two electron beam guns : a 25 kW one to melt the target, a 6 kW one used to heat the specimen. This system also includes a rod feed crucible ; a 10^{-4} Pa vacuum can be achieved. Different deposition parameters such as gun powder, distance between specimen and source, substrate temperature have been studied in order to optimize the deposition conditions. Ingots of different compositions have been cast under vacuum.

In a first step, coatings of S57 and S77 alloys (refer to Table I) have been deposited on different substrates. Heating the substrate above 700°C was necessary to get a good adherence of the coating. Composition analysis has shown that no tantalum was present in the evaporated layer.

In a second step, coatings of Co-Cr-Al-Y and Ni-Cr-Al-Y alloys (refer to Table I) have been deposited on INCO 738, FSX 414 and MAR.M.200+Hf. In a first attempt, coatings without yttrium have been obtained. Afterwards, small ingots of yttrium rich alloys were cast so that the molten pool could be enriched in yttrium. The coating composition, especially its yttrium content, was then similar to that of the feed ingot.

TABLE I

wt% Alloy	Co	Cr	Al	Ni	Ta	Y
S57 Ingot	56,6	25,6	2,8	10,0	5,0	0,5*
S77 Ingot	62,2	25,4	7,3	9,9	5,1	0,5*
CoCrAlY Ingot	64,1	25,2	11,4	-		0,2

* These yttrium contents have not been analyzed.

These coatings have been subjected to oxidation and corrosion tests. The heavily corroded zones which could be observed corresponded to defects in the overlay (tapered nodules, spits,.).

Recently, S57 coatings have been deposited at CRM by the sputtering technique. The deposit structure is shown in Figure II1. It can be compared with that of similar deposits obtained by thermal evaporation (Figure II2a et II2b).

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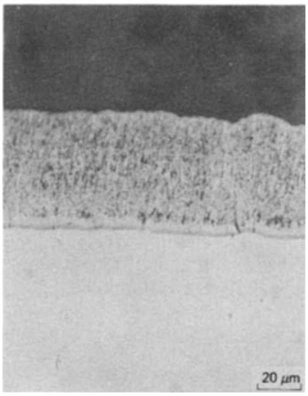

Fig. II-1 – Microstructure of a S 77 sputtered layer deposited at low substrate temperature.

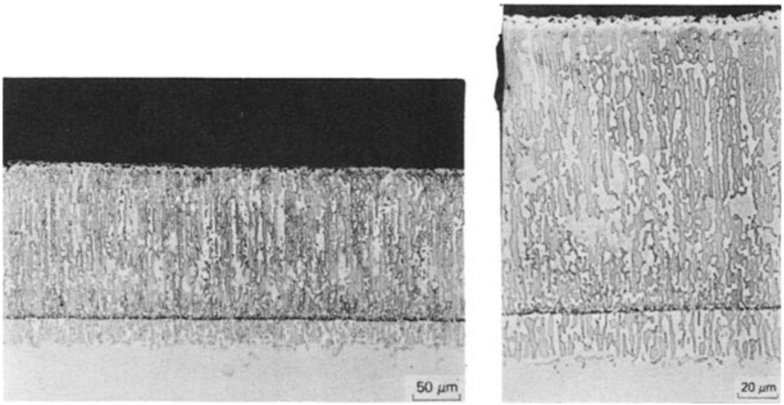

Fig. II-2 – Microstructure of a Co,Cr,Al,Y coating (electron beam vapor deposition).

APPENDIX III (from G. ARTHUR)

Protective coatings by plasma deposition (UK 11)

In industrial gas turbines, temperatures are lower (850°C to 950°C) than in aircraft turbines and oxidation is not a problem. There is thus a need to develop coatings which can resist hot corrosion in the temperature range 800°C to 950°C. Alloys based on Co-Cr were selected as the most promising for development of hot, corrosion-resistant coatings. The plasma spraying process was preferred as the method of application because of its relatively low cost and its flexibility with regard to coating composition.

In the first phase of the project several previously developed cobalt-based alloys (e.g. X-40 and S-57) were used as coatings. The results of this work indicated that alloying elements such as Al, Y and Ta which readily form stable oxides, promoted laminations and porosity in the coating which allowed ingress of corrodants. There was also some evidence that alloys with a high tungsten content had inferior hot corrosion resistance. Therefore in subsequent work these alloying elements were eliminated or greatly reduced. To achieve good bonding between coating and substrate it was found that a high temperature (1050°C) vacuum anneal was required. As this was an added cost in the process and could also affect substrate structure, methods of improving coating-substrate adhesion in the as-sprayed condition were investigated. The outcome of this work was the addition to the base cobalt-chromium alloys of silicon and boron which on oxidation produce glass-forming oxides that dissolve surface oxides formed during the spraying process. Coatings of these modified alloys were found to be of low porosity and adhered well to the substrate in the as-sprayed condition. The aim of the IRD program was to evaluate the hot corrosion resistance of the coatings and to determine their effect on the mechanical properties of the substrate. Two nickel-based superalloys, IN 100 and IN 738 were coated by plasma spraying with the following two alloys :

	%Cr	%Ni	%Al	%Si	%B	%Co
Alloy 1	25	10	3	3	2.3	Bal
Alloy 2	30	10	-	3	2.3	Bal

Typical coating thicknesses were 0.25 mm. For purposes of comparison some specimens with commercial aluminide and LDC-2 coatings were also tested.

Coated and uncoated specimens were subjected to the following tests :

- Burner rig tests (with or without vanadium additive)
- Electrochemical tests
- Mechanical tests

To simulate long term exposure some coated specimens were heated to 850°C for 5000 hrs before testing.

There was little difference between the corrosion resistance of alloy 1 and alloy 2 in a vanadium free environment. The post-coating heat treatment, had a slightly beneficial effect on corrosion resistance (Fig. III1). Where failure had occurred, it appeared to be as a result of substrate corrosion through cracks or other defects in the coatings, the coatings on IN 738 LC performing markedly better than those on the more hot corrosion susceptible IN 100. In the burner rig tests using fuel containing vanadium. The alloy 1 coating contaning 3% aluminum afforded considerably more protection in this test than the aluminum-free alloy 2 coating. In burner tests involving only sodium and sulphur contamination, the sprayed coatings generally afforded greater protection than commercial LDC-2 and aluminide coatings. In the more severe burner tests (with additional vanadium contamination) and in the electrochemical tests, the sprayed coatings were however inferior to the aluminide and LDC-2 coatings.

The coatings had no significant effect on the high cycle fatigue properties of IN 738 LC. In the case of the stress rupture tests insufficient results were obtained to allow firm conclusions to be drawn. With IN 100 it is possible that sprayed coatings after prolonged heat treatment reduce stress-rupture life.

Heating of coated specimens at 850°C in air affected the structure of the substrate to a depth of 120 µm, the plate-like precipitates appearing in the substrate strongly resembling σ phase (Fig. III2).

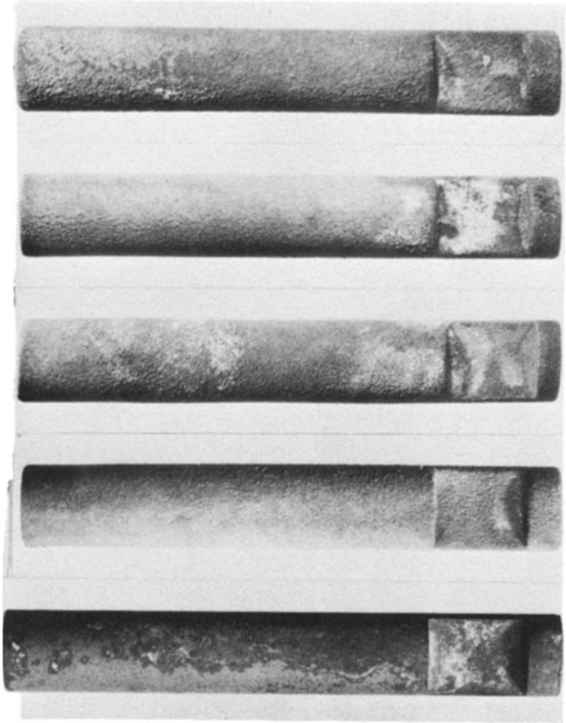

Fig. III-1 – Specimens after NPL burner rig test.

Fig. III-2 – Coated specimen showing plate-like precipitates in IN 738 substrate after 1000 hrs at 850°C.