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AGARD LECTURE SERIES No. 106

# Materials Coating Techniques





NORTH ATLANTIC TREATY ORGANIZATION



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NORTH ATLANTIC TREATY ORGANIZATION

ADVISORY GROUP FOR AEROSPACE RESEARCH AND DEVELOPMENT

(ORGANISATION DU TRAITE DE L'ATLANTIQUE NORD)

AGARD Lecture Series No.106

# MATERIALS COATING TECHNIQUES

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## FOREWORD

In recent years, many new coating techniques have been coming into use, or are being developed, for applications where increased protection of engineering materials from the effects of corrosion, erosion and wear, particularly at high temperatures, is needed. This Lecture Series will be introduced with a review of the principles and the present state-of-the-art of applying metallic, ceramic and organic layers for these purposes, with particular emphasis on new techniques such as plasma spray, ion beam, laser etc. The resultant structure and properties of the coating layers and their interaction with the bulk material will be considered.

Lectures will also cover the behaviour of coated parts, as determined by the coating technique and material, and the effects in service of such aspects as corrosion, fatigue, tribology problems, structural stability etc. Finally, available techniques for the analysis and non-destructive evaluation of the composition, properties and soundness of the layers will be assessed.

D.G.TEER
Lecture Series Director

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# Materials Coating Techniques - Introduction

by

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In general, components used in engineering applications must possess the appropriate structural characteristics to provide stiffness or flexibility, and to carry the applied loads without macroscopic failure. Such properties are associated with the bulk material of the component. Further, the component must have the surface properties necessary for its efficient functioning over the required lifetime. Such properties include electrical, optical and thermal characteristics, but here we will be more concerned with those properties affecting the useful life of the component i.e. corrosion and wear resistance, together with the frictional properties. It is often impossible to obtain the necessary bulk and surface properties if the component is constructed from a single material, and where such a solution is possible, it is usually uneconomic. Thus the bulk of our engineering component should be constructed from as cheap a material as possible, in good supply, which can provide the necessary structural properties, and it should be coated to provide the required surface characteristics. Commonplace examples are mild steel components electroplated with chromium to prevent corrosion. However, modern technology is now making much greater demands. Turbine blades are required to operate at ever higher temperatures, cutting tools are required to remove metal at higher rates, and bearings must operate with minimal wear and low friction over long periods in hostile environments without conventional lubricants. Together with these technological demands we are faced with the very reasonable requirements that we should not further pollute our environment and that our diminishing material resources should be eked out as economically as possible. These are challenges faced by all scientists, engineers and designers but it is certain that they will only be solved satisfactorily with the help of surface coatings. Already considerable achievements and advances have been made in the field of protective coatings, and it is the object of this Lecture Series to present an account of the present state of the art in a range of coating techniques and also to describe how these techniques are presently being applied.

The techniques covered could be described as "modern" in that, although most of them have been with us for a long time, they have been the subject of much recent development and are achieving results which have only recently become possible. These include the exceptionally hard,wear resistant coatings deposited by both Chemical and Physical Vapour Deposition which are sufficiently adherent to the substrate to resist very severe stressing, for example, when used as coatings for cutting tools. They include the highly complex alloy compositions which are now deposited as a routine production process onto turbine blades by P.V.D. Electrodeposition, the oldest and most widely used coating technique, is the subject of continued development and improvement, and one example, the electrodeposition of aluminium for the corrosion protection of high strength steels is included. Recent improvements in sprayed coatings, are described, particularly the densification and improvement in structure that is now achieved. Also included is one truly new technique, that of Laser Surface Alloying. This is already achieving impressive results and will undoubtedly be the subject of much further development, probably in combination with other coating techniques.

In a short series of lectures such as this,it is not possible to cover all techniques. For example,not included are techniques for applying organic coatings. Welding has widespread use as a coating process and is not included. More importantly, it has not been possible to present sputtering as a separate technique. However it is included under the more general heading of Physical Vapour Deposition, and the very significant recent developments will be mentioned briefly. Also, the very wide range of surface modification techniques from carburising, nitriding, through to ion implantation are not included. Although the aim of these techniques e.g. improvement in corrosion and wear resistance, is much the same as for coating techniques, they are different in principle and in practise.

Finally, looking into the future, inevitably there must be a rapid expansion in the use of coatings. This will involve the development of production equipment to handle and coat both large components and large numbers of small components in a reliable and economic manner. Development and improvement of the coatings themselves, their adhesion, their structure, their composition must continue. Concurrent with these developments, it is probable that the techniques used in surface coatings will be extended to be used as novel methods to produce self supporting items, with unusual material properties. Also, and this is most important, the coating process must be accepted as a production process, just as machining, cold or hot forming are presently accepted, and the product should be designed from the start,with the coating and the coating technique in mind. It is hoped that this Lecture Series will produce a better understanding and appreciation of the wide range of coating techniques now available and of the properties of the coatings leading to improved product performance and the more efficient use of materials.

# HIGH RATE PHYSICAL VAPOR DEPOSITION PROCESSES

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## Summary

This paper reviews the Physical Vapor Deposition processes. They are Evaporation, Ion Plating, and Sputtering. The deposition of metals, alloys, intermetallic compounds, and refractory compounds by these processes is discussed. The evolution of the microstructure and the influence of process parameters such as deposition temperature and gas pressure is presented and illustrated with examples. Texture and residual stresses in the deposit are considered.

## Introduction

High technology today demands combinations of diverse properties from a material which is generally unobtainable from a single or monolithic material. Coating technology has advanced rapidly in the past twenty years and it has greatly assisted in meeting such complex demands placed on materials. The important coating methods for high technology applications are plasma and detonation gun spraying techniques, electrodeposition, chemical vapor deposition (CVD), and physical vapor deposition (PVD) processes.

Chemical vapor deposition (CVD) is generally defined as the deposition of a solid material onto a (usually) heated substrate as a result of chemical reactions in the gas phase. These reactions may occur on, at, or near the substrate surface.

On the other hand, physical vapor deposition (PVD) processes which are originally applied to the deposition of single materials such as metals did not involve chemical reactions. The versatility of the PVD processes led to the development of PVD processes for the deposition of compounds which necessarily involve chemical reactions. Thus, the distinction between CVD and PVD processes becomes less sharp.

A unique attribute of PVD processes is that the coating is not the result of a process such as solidification where the laws of physical chemistry govern. They are "non-equilibrium" processes such that any coating may be deposited onto virtually any substrate.

Physical vapor deposition (PVD) technology consists of the techniques of evaporation, ion plating, and sputtering. It is used to deposit films and coatings or self-supported shapes such as sheet, foil, tubing, etc. The thickness of the deposits can vary over a wide variety of applications from decorative to utilitarian over significant segments of the engineering, chemical, nuclear, microelectronics, and related industries.

PVD technology is very versatile, enabling one to deposit virtually every type of inorganic materials - metals, alloys, compounds and mixtures thereof, as well as some inorganic materials. The deposition rates can be varied from 10 to 250,000 Å ($10^{-3}$ to 25 μm) per mirute, the higher rates having come about in the last 20 years with the advent of electron beam heated sources.

The thickness limits for thin and thick films are somewhat arbitrary. A thickness of 10,000 Å (1 μm) is often accepted as the boundary between thick and thin films. A recent viewpoint is that a film can be considered thin or thick depending on whether it exhibits surface-like or bulk-life properties.

## History of PVD Technology

Historically, the first evaporated thin films were probably prepared by Faraday [1] in 1857 when he exploded metal wires in vacuum. The deposition of thin metal films in vacuum by Joule heating was discovered in 1887 by Nahrwold [2] and was used by Kundt [3] in 1888 to measure refractive indices of such films. In the ensuing period, the work was primarily of academic interest being concerned with optical phenomena associated with thin layer of metals, researches into kinetics and diffusion of gases, and gas-metal reactions [4,5]. The application of these technologies on an industrial scale had to await the development of vacuum techniques and therefore dates to the post World War II era, i.e., 1946 and onwards. This proceeded at an exponential pace in thin films and is covered in an excellent review by Glang [6] on evaporated films and in other chapters of the Handbook of Thin Film Technology [7] as well as in the classic text by Holland [8], which reflects the tremendous amount of pioneering work done by that author. A more recent reference on the Science and Technology of Surface Coatings [9] includes material on PVD techniques as well as the other techniques for surface coatings. The work on mechanical properties of thin films has been reported in several review articles [10-15]

The ion plating technique as such, was first reported by Mattox [16,17] in 1963. A similar technique had previously been described by Berghaus [18] who claimed that the coating had "a perfect structure and adhering strength" even for thicker layers. However, it was the results reported by Mattox that stimulated the considerable interest in, and the development of, the process which has since taken place. Mattox [16,17] claimed that the technique produced films with excellent adhesion, even in those cases where the film and substrate materials were mutually insoluble. Further, the films were uniform with no build up at sharp corners and out of line of surface surfaces were also coated. These

results have since been confirmed by many investigators [19-23]. The technique has been further developed and it is now possible to coat metallic or insulating substrates with pure metals, alloys [20], or ceramics [23], and all combinations appear to have very good adhesion.

The first observation of metal deposits sputtered from the cathode of a glow discharge was reported in 1852 by Grove [8]. This original article is worth reading if one wants to appreciate fully the progress which has been made in this field since then.

The history of sputtering can probably be traced most rapidly by reading a selection of survey articles which show this field in its proper perspective in time and corresponding state of physics knowledge [25-29]. In the last twenty years, sputtering and its applications have enjoyed an exponential growth rate with apparatus, process modifications, scientific understanding, and applications in a healthy admixture as in the case with the other PVD techniques.

The work on the production of full-density coatings on self-supported shapes by high deposition rate PVD processes started around 1961 independently at two places in USA. Bunshah and Juntz at the Lawrence Livermore Laboratory of the University of California produced very high purity beryllium foil [30-35], titanium sheet [36], and studied the variation of impurity content, microstructure, and mechanical properties with deposition conditions, thus demonstrating that the microstructure and properties of PVD deposits can be varied and controlled. At about the same time, Smith and Hunt were working at Temescal Metallurgical Corporation in Berkeley, California, on the deposition of a number of metals, alloys, and compounds, and reported their findings in 1964 [36,37]. In the USSR, work on deposition of thin and thick films appear to have started also in the early 1960's primarily at the Kharkov Polytechnique Institute by Professor Palatnik and coworkers, and later at the Paton Electric Welding Institute in Kiev under Professor Movchan and Academician Paton. In the years between 1962 and 1969, there was considerable effort on the part of various steel companies to produce Aℓ and Zn coatings on steel using HRPVD techniques on a production scale [38,39]. In 1969, Airco Temescal Corporation decided to manufacture Ti-6Aℓ-4V alloy foil in pilot production quantities for use in honeycomb structures on the SST aircraft. The project was eminently successful but the patient, the supersonic transport aircraft "SST" died. The results of this work were published in 1970 [40]. To give some idea of the production capability, 1200 ft. per run of Ti-6Aℓ-4V foil, 12" wide, 0.002" thick was be produced at the rate of 2-3 ft. per minute. The stated cost at that time was about 1/5 of the cost for similar material produced by rolling (i.e., $60/lb. for HRPVD vs. $300/lb. for rolled material). It is very difficult to roll this alloy because it work-hardens very rapidly, and therefore needs many annealing cycles to be reduced to thin gauge (A.B. Sauvegot, TMCA Tech. Report AMFL-TR-67-386, December 1967).

The work on thick films and bulk deposits has matured later than the work on thin films and reviews on it have been given by Bunshah [41] and by Paton, Movchan, and Demchishin [42] who summarized the work done at the Paton Electric Welding Institute up to 1973. In addition, the Soviet literature has numerous references to the very extensive work on thin and thick films by Palatnik and coworkers of the Kharkov Polytecnique Institute although this writer cannot cite a review paper from this source. Note should also be made of a recent book in German on electron beam technology by Schiller, and Heisig in which many of the PVD aspects are treated [43].

More recently, thick films and bulk deposits are also being produced by the ion plating and sputtering processes. Developments in all three PVD processes are very rapid and considerable benefit is gained by their commonality and interactive features.

## PVD Processes

### 1. Preamble

In general, deposition processes may be divided into two types: 1) those involving droplet transfer such as plasma spraying, arc spraying, wire-explosion spraying, detonation gun coating; and 2) those involving an atom-by-atom transfer mode such as the physical vapor processes of evaporation, ion plating, and sputtering, chemical vapor deposition, and electrodeposition. The chief disadvantage of the droplet transfer process is the porosity in the final deposit which effects the properties.

There are three steps in the formation of any deposit:

i. Synthesis of the material to be deposited
   a) Transition from a condensed phase (solid or liquid) to the vapor phase,
   b) For deposition of compounds, a reaction between the components of the compound some of which may be introduced into the chamber as a gas or vapor.

ii. Transport of the vapors between the source and substrate.

iii. Condensation of vapors (and gases) followed by film nucleation and growth.

There are significant differences between the various atom transfer processes. In chemical vapor deposition and electrodeposition processes, all of the three steps mentioned above take place simultaneously at the substrate and cannot be independently controlled. Thus, if a choice is made for a process parameter such as substrate temperature (which governs deposition rate in CVD), one is stuck with the resultant microstructure and properties. On the other hand, in the PVD processes, these steps (particularly steps 1 and 3) can be independently controlled and one can therefore have a much greater degree of flexibility in controlling the structure and properties and deposition rate. This is a very important consideration.

### 2. PVD Processes

There are three physical vapor deposition processes, namely evaporation, ion plating, and sputtering.

In the evaporation process, vapors are produced from a material located in a source which is heated by radiation, eddy currents, electron beam bombardment, a laser beam or an electrical discharge. The process is usually carried out in vacuum (typically $10^{-5}$ to $10^{-6}$ torr) so that the evaporated atoms undergo an essentially collisionless line-of-

sight transport prior to condensation on the substrate. The substrate is usually at ground potential (i.e., not biased).

Figure 1 is a schematic of a vacuum evaporation system illustrating electron beam heating. It may be noticed that the deposit thickness is greatest directly above the center-line of the source and decreases away from it [44]. This problem is overcome by imparting a complex motion to substrates (e.g., in a planetary or rotating substrate holder) so as to even out the vapor flux on all parts of the substrate, or by introducing a gas at a pressure of 5 to 200 μm into the chamber so that the vapor species undergo multiple collisions during transport from the source to the substrate, thus producing a reasonably uniform (± 10%) thickness of coating on the substrate. The latter technique is called gas-scattering evaporation or pressure plating [45,46].

In the ion plating process, the material is vaporized in a manner similar to that in the evaporation process but passes through a gaseous glow discharge on its way to the substrate, thus ionizing some of the vaporized atoms (see Figure 2). The glow discharge is produced by biasing the substrate to a high negative potential (0.2 to 5 kV) and admitting a gas, usually argon, at a pressure of 5 to 200 μm into the chamber. In this simple mode, which is known as diode ion plating, the substrate is bombarded by high energy gas ions which sputter off the material present on the surface. This results in a constant cleaning of the substrate (i.e., a removal of gaseous impurities by sputtering) which is desirable for producing better adhesion and lower impurity content. On the other hand, it produces the undesirable effects of decreasing the deposition rates since some of the substrate is sputtered off, as well as causing a considerable (and often undesired) heating of the substrate by intense gas ion bombardment. The latter problem can be alleviated by using the supported discharge ion plating process [47a,b] where the substrate is at a lower negative potential, the electrons necessary for supporting the discharge coming from an auxillary heated tungsten filament. The high gas pressure during deposition causes deposition of all surfaces due to gas scattering as discussed above, although the deposit thickness varies from front to back of the substrate.

In the sputtering process, illustrated schematically in Figure 3, positive gas ions (usually argon ions) produced in a glow discharge (gas pressure 20 to 150 μm) bombard the target material (also called the cathode) dislodging groups of atoms which then pass into the vapor phase and deposit onto the substrate.

The recent development of a class of sputtering sources with magnetic plasma confinement, called magnetrons, and of high performance triodes, is greatly enhancing the capabilities of the sputtering process.

Magnetrons can provide an order of magnitude increase in deposition rate over that of planar diodes. They also can provide uniform deposition over very large substrate areas (many $m^2$). In addition, well designed magnetrons virtually eliminate substrate heating due to electron and plasma bombardment.

Deposition rates for magnetrons and high performance triodes can be equivalent to those used in electroplating and are high enough to make thick coatings and free standing shapes feasible. For example, high rate triode sputtering has been used to make a free standing 1.3 Kg deposit of Cu-alloy in the form of a cylinder 15 cm. in diameter.

Alternate geometries are of importance in various processing applications. For example, the hollow cathode sputtering would be the ideal geometry for coating the outer surface of a wire.

Sputtering is an inefficient way to induce a solid-to-vapor transition. Typical yields (atoms sputtered per incident ion) for a 500 eV argon ion incident on a metal surface are unity. Thus the phase change energy cost is from 3 to 10 times larger than evaporation [48]. Thornton [48] has provided an excellent review on sputtering as it applies to deposition technology. The reader is also referred to the proceedings of a special conference on sputtering and ion plating [49].

The deposition rates for the various processes are indicated in Table I. It should be noted that sputtering rates at the high side (approximately 10,000 Å/min.) can only be obtained for target materials of high thermal conductivity like copper, since heat extraction from the target is the limiting parameter. For most materials, it is much lower, i.e., 500 to 1000 Å/min.

3. Advantages and Limitations

There are several advantages of PVD processes over competitive processes such as electrodeposition, CVD, plasma spraying. They are:

1. Extreme versatility in composition of deposit. Virtually any metal, alloy, refractory, or intermetallic compound, some polymeric type materials and their mixtures can easily be deposited. In this regard, they are superior to any other deposition process.
2. The substrate temperature can be varied within very wide limits from subzero to high temperatures.
3. Ability to produce coatings or self-supported shapes at high deposition rates.
4. Deposits have very high purity.
5. Excellent bonding to the substrate.
6. Excellent surface finish which can be equal to that of the substrate.
7. Elimination of pollutants and effluants from the process which is a very important ecological factor.

The present limitations of PVD processes are:

1. Inability to deposit polymeric materials with certain exceptions.
2. Higher degree of sophistication of the processing equipment and hence a higher initial cost.
3. Relatively new technology and the "mystique" associated with vacuum processes, much of which is disappearing with education and familiarity.

Deposition of Various Materials

The family of materials which are deposited by evaporation include metals, semiconductors, alloys, intermetallic compounds, refractory compounds (i.e., oxides carbides, nitrides, borides, etc.) and mixtures thereof. An important point is that the source material should be pure and free of gases and/or inclusions to forestall the problems of molten droplet injection from the pool commonly called spitting.

Let us consider each of the materials.

1. Deposition of Metals and Elemental Semiconductors

Evaporation of single elements can be carried out from a variety of evaporation sources subject to the restrictions discussed above dealing with melting point reactions with container, deposition rate, etc. A typical arrangement is shown in Figure 1 for electron beam heating. As discussed above, either heating methods can also be used. These are the simplest materials to evaporate. Fortunately, at this time, it is estimated that 90% of all the materials evaporated is aluminum!

2. Deposition of Alloys

Alloys consist of two or more elements , which have different vapor pressures and hence different evaporation rates. As a result, the vapor phase and therefore the deposit has a constantly varying composition. There are two solutions to this problem: multiple sources and single rod-fed or wire-fed electron beam source.

a) Multiple Sources

This is the more versatile system. The number of sources evaporating simultaneously is equal to or less than the number of constituents in the alloy. The material evaporated from each source can be a metal, alloy or compound. Thus, it is possible to synthesize a dispersion strengthened alloy;e.g., Ni-$ThO_2$. On the other hand, the process is complex because the evaporation rate from each source has to be monitored and controlled separately. The source to substrate distance would have to be sufficiently large (15 inches for 2 inch diameter sources) to have complete blending of the vapor streams prior to deposition, which decreases the deposition rate (See Figure 4). Moreover, with gross difference in density of two vapors, it may be difficult to obtain a uniform composition across the width of the substrate due to scattering of the lighter vapor atoms.

It is also possible to evaporate each component sequentially thus producing a multilayered deposit, which is then homogenized by annealing after deposition. This procedure makes it even more difficult to get high deposition rates.

b) Single Rod Fed Electron Beam Source

The disadvantages of multiple sources for alloy deposition can be avoided by using a single source [50]. They can be wire-fed or rod-fed sources, the latter being shown in Figure 5. There is a molten pool of limited depth above the solid rod. If the components of an alloy, $A_1B_1$, have different equilibrium vapor pressures, then the steady state composition of the molten pool will differ from the feed rod, e.g. $A_1B_{10}$. Under steady state conditions, the composition of the vapor is the same as that of the solid being fed into the molten pool. One has a choice of starting with a button of appropriate composition $A_1B_{10}$ on top of a rod $A_1B_1$ to form the molten pool initially or one can start with a rod of alloy $A_1B_1$ and evaporate until the molten pool reaches composition $A_1B_{10}$. Precautions to be observed are that the temperature and volume of the molten pool have to be constant to obtain a constant vapor composition. A theoretical model has been developed and confirmed by experiment. Ni-20Cr, Ti-6Aℓ-4V, Ag-5Cu, Ag-10Cu, Ag-20Cu, Ag-30Cu, Ni-xCr-yAℓ-zY alloy deposits have been successfully prepared. To date, experimental results indicate that this method can be used with vapor pressure differences of a factor of 5000 between the components. This method cannot be used where one of the alloy constituents is a compound, e.g., Ni-$ThO_2$.

3. Deposition of Intermetallic Compounds

Intermetallic compounds which are generally deposited such as GaAs, PbTe, InSb, etc. have as their constituents elements with low melting points and high vapor pressures. These compound semiconductors need to have a carefully controlled stoichiometry, i.e., cation:anion ratio. Therefore they can best be prepared by flash evaporation or sputtering.

In flash evaporation, powder or chips of the two components are sprinkled onto a superheated sheet to produce complete evaporation of both components. Various possible arrangements are used.

4. Deposition of Refractory Compounds

Refractory compounds are substances like oxides, carbides, nitrides, borides, sulphides which characteristically have a very high melting point (with some exceptions). In some cases, they form extensive defect structures,i.e., exist over a wide stoichiometric range. For example, in TiC, the C/Ti ratio can vary from 0.5 to 1.0,demonstrating vacant carbon lattice sites. In other compounds, the stoichiometric range is not so wide.

Evaporation processes for the deposition of refractory compounds are further subdivided into two types: 1. Direction Evaporation [51] where the evaporant is the refractory compound itself; 2. Reactive Evaporation [52] or activated reactive evaporation (ARE) [53] where a metal or a low valency compound of metal is evaporated in the presence of a partial pressure of a reactive gas to form a compound deposit, e.g., where Ti is evaporated in the presence of $N_2$ to form TiN or where Si or SiO is evaporated in the presence of $O_2$ to form $SiO_2$.

a) Direction Evaporation

Evaporation can occur with or without dissociation of the compound into fragments. The observed vapor specie show that very few compounds evaporate without dissocation. Examples are SiO, $MgF_2$, $B_2O_3$, $CaF_2$, and other Group IV divalent oxides (SiO homologs like GeO and SnO).

In the more general case, when a compound is evaporated or sputtered the material is not transformed to the vapor state as compound molecules but as fragments thereof. Subsequently, the fragments have to recombine most probably on the substrate to reconstitute the compound. Therefore, the stoichiometry (anionication ratio) of the deposit depends on several factors including the deposition rate and the ratios of the various molecular fragments, the impingement of other gases present in the environment, the surface mobility of the fragments (which in turn depends on their kinetic energy and substrate temperature), the mean residence time of the fragments of the substrate, the reaction rate of the fragments on the substrate to reconstitute the compound and the impurities present on the substrate. For example, it was found that direct evaporation of $Al_2O_3$ resulted in a deposit which was deficient in oxygen, i.e., which had the composition $Al_2O_{3-x}$ [54]. This $O_2$ deficiency could be made up by introducing $O_2$ at a low partial pressure into the environment.

b) Reactive Evaporation

In reactive evaporation [52], metal or alloy vapors are produced in the presence of a partial pressure of reactive gas to form a compound either in the gas phase or on the substrate as a result of a reaction between the metal vapor and the gas atoms, e.g.,

$$2Ti + C_2H_2 \rightarrow 2TiC + H_2$$

The reaction may be encouraged to go to completion by activating and/or ionizing both the metal and gas atoms in the vapor phase. It is called the Activated Reactive Evaporation Process [53], as illustrated in Figure 6. In this process, the metal is heated and melted by a high acceleration voltage electron beam. The melt has a thin plasma sheath on top of the melt. The low energy secondary electrons from the plasma are pulled upwards into the reaction zone by an electrode placed above the pool biased to a low positive d.c. potential (20 to 100 V). The low energy electrons have a high ionization cross-section, thus ionizing or activating the metal and gas atoms and increasing the reaction probability on collision. The synthesis of TiC by reaction of Ti metal vapor and $C_2H_2$ gas atoms with a carbon/metal ratio approaching unity was achieved with this process [53,55]. Moreover, by varying the partial pressure of either reactants, the carbon/metal ratio of carbides could be varied [56] at will. The ARE process has also been recently applied to the synthesis of all the five different Ti-O oxides [53]. These authors noted that in the ARE process (i.e., with a plasma) as compared to the RE process (i.e., without a plasma) a higher oxide formed for the same partial pressure of $O_2$ thus demonstrating a better utilization of the gas in the presence of a plasma. The same observation was noticed by Bunshah and Raghuram [53] as well as by Granier and Besson [57] for the deposition of nitrides.

It should be pointed out that the two processes of Direct Evaporation and Activated Reactive Evaporation are complementary to each other, having their own advantages and limitations.

c) Reactive Ion Plating

Reactive Ion Plating (RIP) is very similar to the reactive evaporation process in that metal atoms and reactive gases react to form a compound aided by the presence of a plasma. Since the partial pressure of the gases in reactive ion plating are much higher ($> 10^{-2}$ torr) than in the ARE process ($10^{-4}$ torr), the deposits can become porous or sooty. The plasma cannot be supported at a lower pressure in the simple diode ion plating process. Therefore Kobayashi and Doi [58] introduced an auxillary electrode biased to a positive low voltage (as originally conceived for the ARE process) to initiate and sustain the plasma at a low pressure ($\sim 10^{-3}$ torr) as shown in Figure 7. This is no different than the ARE process with a negative bias on the substrate reported [41] much earlier by Bunshah and which was designated by him as the Biased ARE or BARE process.

d) Reactive Sputtering

Reactive sputtering is that process where at least one of the coating species enters the system in the gas phase. It is illustrated in Figure 8. Examples of reactive sputtering include sputtering Al in $O_2$ to form $Al_2O_3$ [59], Ti in $O_2$ to form $TiO_2$ [60], In-Sn in $O_2$ to form tin-doped $In_2O_3$ [61], Nb in $N_2$ to form NbN [62], Cd in $H_2S$ to form CdS [63], In in $PH_3$ to form InP [64], and Pb-Nb-Zr-Fe-Bi-La in $O_2$ to form a ferroelectric oxide [65].

The advantages of reactive sputtering are that: 1) many complex compounds can be formed using relatively easy to fabricate metallic targets; 2) insulating compounds can be deposited using d.c. power supplies; and 3) graded compositions can be formed as described in the preceding section. The difficulty in the reactive sputtering process is the complexity which accompanies its versatility.

## Microstructure of PVD Condensates

### 1. Microstructure Evolution

PVD condensates deposit as single crystal films on certain crystal planes of single crystal substrates, i.e., by epitaxial growth or in the more general case, the deposits are polycrystalline. In the case of films deposited by evaporation techniques, the main variables are: 1) the nature of the substrates; 2) the temperature of the substrate during deposition; 3) the rate of deposition; 4) the deposit thickness. Contrary to what might be intuitively expected, the deposit does not start out as a continuous film one monolayer thick and grow. Instead, three-dimensional nuclei are formed on favored sites on the substrates, e.g., cleavage steps on a single crystal substrate, these nuclei grow laterally and in thickness (the so-called growth state) ultimately impinging on each other to form a continuous film. The average thickness at which a continuous film forms depends on the deposition temperature and the deposition rate (both of which influence the surface mobility of the adatom) and varies from 10 Å for Ni condensed at 15 K to 1000 Å for Au condensed at 600° K. Once a continuous film has formed,

the subsequent evolution to the final structure of the thin film is poorly understood at present. It undoubtedly depends on the factors mentioned above which in turn influence the primary variables of nucleation rate, growth rate, and surface mobility of the adatom. The problem has been tackled by Van der Drift [66], and is also the subject of a paper by Thornton [67].

The microstructure and morphology of thick single phase films have been extensively studied for a wide variety of metals, alloys and refractory compounds. The structural model was first proposed by Movchan and Demchishin [68], Figure 9 and was subsequently modified by Thornton [69] as shown in Figure 10. Movchan and Demchishin's diagram was arrived at from their studies on deposits of pure metals and did not include the transition zone of Thornton's model, Zone T, which is not prominent in pure metals or single phase alloy deposits, becomes quite pronounced in deposits of refractory compounds or complex alloys produced by evaporation, and in all types of deposits produced in the presence of a partial pressure of inert or reactive gas, as in sputtering or ion plating processes.

The evolution of the structural morphology is as follows, as the writer sees it today.

At low temperatures, the surface mobility of the adatoms is reduced and the structure grows as tapered crystallites from a limited number of nuclei. It is not a full density structure but contains longitudinal porosity of the order of a few hundred angstroms width between the tapered crystallites. It also contains a high dislocation density and has a high level of residual stress. Such a structure has also been called "Botryoidal" and corresponds to Zone 1 in Figures 9 and 10.

As the substrate temperature increases, the surface mobility increases and the structural morphology first transforms to that of Zone T, i.e., tightly packed fibrous grains with weak grain boundaries and then to a full density columnar morphology corresponding to Zone 2 (Figure 10).

The size of the columnar grains increases as the condensation temperature increases. Finally, at still higher temperatures, the structure shows an equiaxed grain morphology, Zone 3. For pure metals and single phase alloys, $T_1$ is the transition temperature between Zone 1 and Zone 2 and $T_2$ is the transition temperature between Zone 2 and Zone 3. According to Movchan and Demchishin's original model [68], $T_1$ is 0.3 $T_m$ for metals, and 0.22 - 0.26 $T_m$ for oxides whereas $T_2$ is 0.45 - 0.4 $T_m$ for both ($T_m$ is the melting point in K).

Thornton's modification shows that the transition temperature may vary significantly from those stated above and in general shift to higher temperatures as the gas pressure in the synthesis process increases.

It should be emphasized that:

1. the transition from one zone to the next is not abrupt but smooth. Hence the transition temperature should not be considered as absolute but as guidelines.
2. all zones are not found in all deposits. For example, Zone T is not prominent in pure metals, but becomes more pronounced in complex alloys, compounds, or in deposits produced at higher gas pressures. Zone 3 is not seen very often in materials with high melting points.

Elegant proof of the importance of the adatom surface mobility was also provided by Movchan and Demchishin [68]. Plots of the log of the grain diameter versus the inverse of deposition temperature in Zones 2 and 3 yield straight lines from which activation energies can be computed. It was found that the activation energy for Zone 2 growth corresponded to that for surface self-diffusion and for Zone 3 growth to volume self-diffusion.

The morphological results reported by Movchan and Demchishin for nickel, titanium, tungsten, $Al_2O_3$ and $ZrO_2$ have been confirmed for several metals and compounds [41].

Bunshah and Juntz [70] studied the influence of condensation temperature on the deposition of titanium. Their microstructures, shown in Figure 11 agree substantially with those of Movchan and Demchishin for Zones 1 and 2 and $T_1$, the transition temperature between Zones 1 and 2. However, they failed to observe Zone 3 at temperatures above 700°C, as found by Movchan and Demchishin [68]. The structure was columnar up to 833°C which is the $\alpha:\beta$ phase transformation temperature for titanium. At deposition temperatures above 833°C, the deposit crystallizes as the $\beta$ phase and on cooling to room temperature, should transform to the $\alpha$ phase, resulting in the typical "tranformed-beta" microstructure shown in Figure 11 (900°C deposit), which could be mistaken for an equiaxed microstructure. Hence, the claim of such a transition in structure from Zone 2 to 3 by Movchan and Demchishin is confusing.

Kane and Bunshah [71] observed the change in morphology in deposited-nickel sheet. At 425°C deposition temperature, the deposit showed a Zone 2 morphology, whereas, at 554°C, the deposit showed a Zone 3 morphology.

Chambers and Bower [72] studied the deposition of magnesium, copper, gold, iridium, tungsten, and stainless steel. Of the photomicrographs presented, gold and magnesium showed Zone 2 columnar morphology at the appropriate substrate temperatures.

Ni-20Cr sheets were deposited by Agarwal, Kane and Bunshah [73]. At 960°C and 650°C deposition temperatures, the surface and cross-section showed an equiaxed Zone 3 morphology. At 427°C deposition temperature, Zone 2 morphology is exhibited.

Mah and Nordin [74] found that the Movchan-Demchishin model was obeyed by beryllium also. They observed structures corresponding to all three zones with transition temperatures as predicted by the model.

Neirynick, Samaey and Van Poucke [75] studied the influence of deposition rate and substrate temperature on the microstructure, adhesion, texture, and condensation mechanism of aluminum and zirconium coatings on steel substrates and wires in batch and continuous coating methods.

Kennedy [76] showed a change in morphology from columnar to equiaxed in Fe and Fe-10Ni alloy with higher deposition temperature. Deposits of Fe-1%Y which is a two

phase alloy, showed columnar morphology only, the structure becoming coarser at higher deposition temperature. The second phase appears to nucleate new grains so that the grain size in Fe-1%Y alloys is much finer than that of iron.

The microstructure of copper-nitrogen alloys [77] produced by codeposition from two sources showed a single phase, as might be expected for this system, which shows a complete solid solubility.

In alloy systems showing the presence of several phases, e.g., Ni-B and Cr-Si, the deposits showed the phases present corresponded to those expected from the phase diagram[77].

Smith, Kennedy, and Boericke [40] studied the deposition of the two phase ($\alpha+\beta$) type Ti-6Al-4V alloy deposited from a single rod-fed source. The microstructure was very similar to wrought material with the same characteristic $\alpha+\beta$ morphology present on a finer scale in the deposited material.

Dispersion-strengthened alloys produced by codeposition from multiple sources have also been produced. Paton et al. [77] produced Ni-TiC, Ni-NbC, and Ni-$ZrO_2$ alloys. The particle size increases from 100 Å to 1000 Å by changing the deposition temperature from 350 to 1000°C. The size of the dispersed carbide phase particles increased on annealing and 1000 to 1100°C due to their slight solubility in nickel. On the other hand, the size and distribution of the $ZrO_2$ dispersion remained constant even after exposure at 1200°C for 5 hours.

Movchan, Demchishin, and Kooluck [78] produced Fe-NbC and Fe-Ni-NbC dispersion strenghtened alloys by coevaporation. The microstructure exhibited columnar morphology, with the inclusion of a fine dispersion of NbC particles.

Raghuram and Bunshah [79] studied the microstructure of TiC deposits from 500 to 1450°C, as shown in Figure 12. They observed the transition from the tapered crystallite (Zone 1) to columnar structure at 973 K, or 700°C (0.3 $T_m$). The highest deposition temperature (1450°C) used by these investigators was not sufficient to produce an equiaxed structure although this temperature corresponds to 0.51 $T_m$.

The energy of the depositing beam of atoms can be increased if some of them are ionized. It has been shown by Smith [81] that a small fraction of the vaporized species from an electron beam heated source is ionized due to collisions with electrons in the plasma sheath above the molten pool. Bunshah and Juntz [81] biased the substrate to -5000 V during the deposition of beryllium at 570°C, and found that the columnar grain size was markedly refined by the ion bombardment as compared to the grain size produced without biasing the substrate at the same deposition temperature. It may be postulated that the ion bombardment causes a localized increase in temperature at the surface where deposition is occurring, thus causing a higher nucleation rate and a finer grain size. Similar results have been reported for tantalum [82]. The use of hollow cathode gun intensifies the degree of ionization of the vapor species, resulting in a marked increase in kinetic energy of the vaporized atoms [83]. The effects of substrate bias are, therefore, easier to observe. Increasing the substrate bias results in a change in morphology from columnar to fine, equiaxed grains for silver deposited on beryllium and stainless steel [84], and for silver and copper deposited on stainless steel [85].

On the other hand, the presence of a gas at high pressures (5 to 20 μm) results in a net decrease in kinetic energy of the vaporized atoms due to multiple collisions during the transverse from source to substrate. This degrades the microstructure to loose columnar grains [85] and eventually to an agglomerate of particles. (This in fact is a way to produce fine powders by evaporation and subsequent gas-phase nucleation and condensation.) The negative effects of the presence of a high gas density on the kinetic energy and the mobility of adatoms on the deposit surface can be overcome by either biasing the substrate [85,86] and/or heating the substrate to a higher temperature.

2. Texture

The texture of evaporated deposits is in general dependent on deposition temperature. At low deposition temperatures, a strong preferred orientation is generally observed: {211} in iron [76], {220} in TiC [79], {0002} in Ti [87]. As deposition temperature increases, the texture tends to become more random. In the case of beryllium [84], the texture changed to a $\{11\bar{2}0\}$ orientation at high deposition temperatures. The presence of a gas tends to shift the preferred orientation to high index planes. For silver, increasing the substrate bias changes the preferred orientation from {111} to {200} and back to {111}.

3. Residual Stresses

Residual stresses in deposits are of two types. The first kind arises from the imperfections built in during growth (the so-called growth stresses). An increase in deposition temperature produces a marked decrease in the magnitude of this stress [79,88]. The other source of residual stress is due to the mismatch in the coefficient of thermal expansion between the substrate and the deposit. Its magnitude and size depend on the values of the thermal expansion coefficients as well as the thickness and size of the substrate and deposit. The influence of a negative bias on the substrate produces a compressive stress in the deposit, which reaches a maximum value at -200 to -300 V d.c. bias and then decreases [86].

High residual stresses can cause plastic deformation (buckling or bending), cracking in the deposit or the substrate, or cracking at the substrate-deposit interface. The latter can be minimized by grading the interface, i.e., producing the change in material over a finite distance instead of producing it abruptly at a sharp interface. A graded interface can be produced by gradually changing the deposition conditions or by interdiffusion, which is enhanced by higher substrate temperature or increased kinetic energy of the vapor species.

References


1. M. Faraday, Phil. Trans., 147: 145 (1857).
2. R. Nahrwold, Ann. Physik, 31: 467 (1887).
3. A. Kundt, Ann. Physik, 34: 473 (1888).
4. F. Soddy, Proc. Roy. Soc. London, 78: 429 (1967).
5. I. Langmir, J. Am. Chem. Soc. 35: 931 (1913).
6. R. Glang, in Handbook of Thin Film Technology, (L.I. Maissel and R. Glang, eds.), McGraw Hill, 1970, p. 1-7.
7. L.I. Maissel and R. Glang (eds), Handbook of Thin Film Technology, McGraw Hill, 1970.
8. L. Holland, Vacuum Deposition of Thin Films, Chapman & Hall, 1956.
9. B.N. Chapman and J.C. Anderson (eds), Science and Technology of Surface Coatings, Academic Press, 1974.
10. J.A. Allen, Rev. Pure Appl. Chem. 4: 133 (1954).
11. G.A. Bassett and D.W. Pashley, J. Inst. Metals 87: 449 (1958).
12. R.W. Hoffman, Thin Films, American Society for Metals, 1964, p. 99.
13. R.W. Hoffman, Physics of Thin Films, 3: 246 (1966).
14. W. Buckel, J. Vac. Sci. Technol. 6: 606 (1969).
15. K. Kinosita, Thin Solid Films, 12: 17 (1972).
16. D.M. Mattox, Sandia Corporation Report, SC-DR-281-63 (1963).
17. D.M. Mattox, J. Appl. Phys. 34: 2493 (1963).
18. B. Berghaus, U.K. Patent Specification, 510.993 (1938).
19. T. Spalvins, J.S. Przybyszeski, and D.H. Buckley, NASA-TND-3707 (1966).
20. D.L. Chambers, and D.C. Carmichael, Research/Development Mag. 22: 32 (1971).
21. D.M. Mattox, J. Vac. Sci. Technol. 10: 47 (1973).
22. D.G. Teer, Tribology, 8: 247 (1975).
23. J. Chin, and N.B. Elsner, Proc. 5th Int. Conf. C.V.D. 241 (1975).
24. G.W. White, Research/Development Mag. 24: 43 (1973).
25. E. Kay, Advan. Electron. Electron. Phys. 17: 245 (1973).
26. L.I. Maissel, Physics of Thin Films, 3: 61 (1966).
27. M.H. Francombe, Basic Problems in Thin Film Physics, Vandenhoeck and Ruprecht, Goettingen, 1966, p. 52.
28. K.L. Chopra, Thin Film Phenomena, McGraw Hill Book Company, NY., 1969.
29. J.D. Cobine, Gaseous Conductors: Theory and Engineering Applications, Dover Publications, Inc., NY., 1958, p. 205.
30. R.F. Bunshah, Physical Metallurgy of Beryllium, April 1963, Conf. No. 170b, Oak Ridge National Laboratory.
31. R.F. Bunshah, in Materials Science and Technology for Advanced Applications, Vol. II., American Society for Metals, 1964, p. 31.
32. R.F. Bunshah, Metals Engineering Quarterly, Nov. 1964, p. 8.
33. R.F. Bunshah and R.S. Juntz, in Beryllium Technology, Vol. 1, Gordon and Breach Science Publishers, 1966, p. 1.
34. R.F. Bunshah, Proceedings Int. Conf. on Beryllium, Grenoble, France, Press Universitaires de France, 1965, p. 63.
35. R.F. Bunshah and R.S. Juntz, Trans. Vac. Met. Conf., American Vacuum Society, 1966, p. 209.
36. R.F. Bunshah and R.S. Juntz, Trans. Vac. Met. Conf., American Vacuum Society, 1965, p. 200.
37. H.R. Smith, in Materials Science and Technology for Advanced Applications, Vol. II, American Society for Metals, 1964, p. 569.
38. R.F. Meyers and R.P. Morgan, Trans. Vac. Met. Conf., American Vacuum Society, 1966, p. 271.
39. J.F. Butler, J. Vac. Sci. Tech. 7: S-52 (1970).
40. H.R. Smith, K. Kennedy, and F.S. Boericke, J. Vac. Sci. Tech. 7: 48S (1978).
41. R.F. Bunshah, New Trends in Materials Processing, American Society for Metals, 1976, p. 200.
42. B.A. Paton, B.A. Movchan, and A.V. Demchishin, Proc. 4th Int. Conf. on Vacuum Metallurgy, Iron and Steel Institute of Japan, 1973, p. 251.
43. S. Schiller and U. Heisig, "Evaporation Techniques" (in German), VEB VERLAG TECHNIK, Berlin, 1975.
44. E.B. Graper, J. Vac. Sci. Tech. 8: 333 (1971); and J. Vac. Sci. Tech. 10: 100 (1973).
45. K.D. Kennedy, G.R. Schevermann, H.R. Smith, Jr., Research/Development Mag. 22: 40 (1971).
46. H.A. Beale, R.F. Bunshah, Proc. 4th Int. Conf. on Vac. Met., Iron and Steel Institute of Japan, 1973, p. 238.
47. C.T. Wan, D.L. Chambers, D.C. Carmichael, ibid, p. 231.
48. J.A. Thornton, SAE Transactions, 1973.
49. "Sputtering and Ion Plating", NASA SP-511, 1972.
50. R. Nimmagadda, A.C. Raghuram and R.F. Bunshah, J. Vac. Sci. Tech. 9: 1406 (1972).
51. B.A. Movchan and A.V. Demchishin, Fizika Metall. 28: 653 (1969).
52. M. Auwarter, U.S. Patent 2,920,002 (1960).
53. R.F. Bunshah and A.C. Raghuram, J. Vac. Sci. Technol. 9: 1385 (1972).
54. D. Hoffman and D. Liebowitz, J. Vac. Sci. Technol. 9: 326 (1972).
55. A.C. Raghuram, R. Nimmagadda, R.F. Bunshah and C.N.J. Wagner, Thin Solid Films 20 187 1974
56. W. Grossklaus and R.F. Bunshah, J. Vac. Sci. Technol. 12: 593 (1975).
57. J. Granier and J. Besson, Proc. 9th Plansee Seminar, Reutte, Austria, May 23-26, 1977.
58. M. Kobayashi and Y. Doi, Thin Solid Films 54: 57 (1978).
59. R.F. Frieser, J. Electrochem. Soc. 113: 357 (1966).
60. K. Wasa and S. Hayakawa, Microelectronics and Reliability 6: 213 (1967).
61. J.A. Thornton and V.L. Hedgcoth, J. Vac. Sci. Technol. 13: 117 (1976).

62. K.S. Keskar, Y. Yamashita, Y. Onodera, Y. Goto, and T. Aso, J. Appl. Phys. 45 3102 (1974).
63. T.K. Lakshmanan and J.M. Mitchell, Proceedings 10th National Vacuum Symposium, 1963, p. 335.
64. J.A. Thornton and A.J. Jonath, "Indium Phosphide Films Deposited by Cylindrical Magnetron Reactive Sputtering," Proceedings 12th IEEE Photovoltaic Specialists Conf., Baton Rouge, Louisiana, 1976.
65. S.F. Vogel and I.C. Barlow, J. Vac. Sci. Technol. 12: 381 (1973).
66. A. Van der Drift, Phillips Res. Rep. 22: 267 (1967).
67. J.A. Thornton, Ann. Rev. Mater. Sci., p. 239.
68. B.A. Movchan and A.V. Demchishin, Fizika Metall. 28: 653 (1969).
69. J.A. Thornton, J. Vac. Sci. Tech. 12: 830 (1975).
70. R.F. Bunshah and R.S. Juntz, Met. Trans. 4: 21 (1973).
71. N. Kane and R.F. Bunshah, in Proceedings of the 4th Int. Conf. on Vacuum Metallurgy, Tokyo, Japan, Iron and Steel Institute of Japan, 1973, p. 242.
72. D.L. Chambers and W.K. Bower, J. Vac. Sci. Technol. 7: S62 (1970).
73. N. Agarwal, N. Kane and R.F. Bunshah, National Vacuum Symposium, NY., 1973.
74. G. Mah and C.W. Nordin, in Proceedings of the 16th Annual Conf., Society of Vacuum Coaters, Chicago, 1973, p. 103.
75. M. Neirynck, W. Samaey, and L. Van Poucke, J. Vac. Sci. Technol. 11: 647 (1974).
76. K. Kennedy, in Transactions of the Vacuum Metallurgy Conference, American Vacuum Society, 1968, p.195.
77. B.A. Paton, B.A. Movchan, and A.V. Demchishin, Proc. 4th Int. Conf. on Vacuum Metallurgy, Iron and Steel Institute of Japan, 1973, p. 251.
78. B.A. Movchan, A.V. Demchishin and L.V. Kooluck, J. Vac. Sci. Technol. 11: 640 (1974).
79. A.C. Raghuram and R.F. Bunshah, J. Vac. Sci. Technol. 9: 1389 (1972).
80. H.R. Smith, in Materials Science and Technology for Advanced Applications, Vol. II, American Society for Metals, 1964, p. 569.
81. R.F. Bunshah and R.S. Juntz, J. Vac. Sci. Technol. 9: 404 (1972).
82. D.M. Mattox and G.J. Kominiak, J. Vac. Sci. Technol. 9: 528 (1972).
83. J. Morley and H.R. Smith, J. Vac. Sci. Technol. 9: 1377 (1972).
84. G. Mah, P.S. McLeod, and D.G. Williams, J. Vac. Sci. Technol. 11: 663 (1974).
85. W.R. Stowell and D. Chambers, J. Vac. Sci. Technol. 11: 653 (1974).
86. R.D. Bland, G.J. Kominiak and D.M. Mattox, J. Vac. Sci. Technol. 11: 671 (1974).
87. C.D. Turk and H.L. Marcus, Trans. AIME 242: 2251 (1968).
88. J.A. Thornton, in New Industries and Applications for Advanced Materials Technology, Vol. 19, SAMPE, 1974, p. 443.

TABLE I

| Process | Deposition Rate (Å $min^{-1}$) |
|---|---|
| Evaporation | 100 - 250,000 (in special cases to 750,000) |
| Ion Plating | 100 - 250,000 |
| Sputtering | 25 - 10,000 |

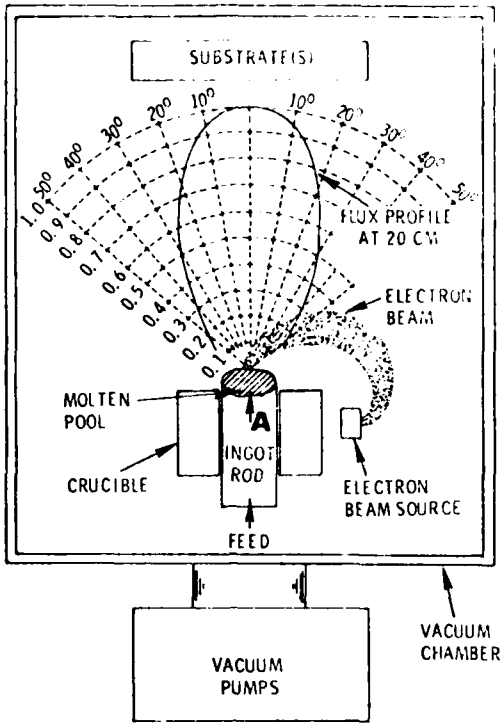



Figure 1. Vacuum evaporation process using electron-beam heating.

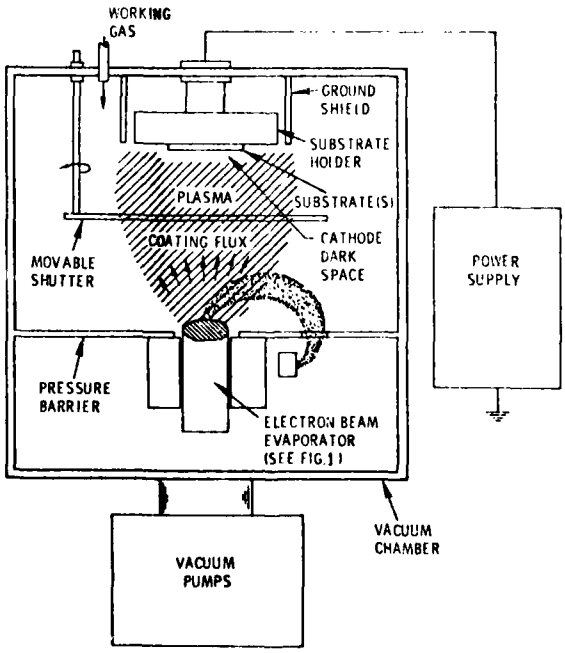



Figure 2. Ion plating process.

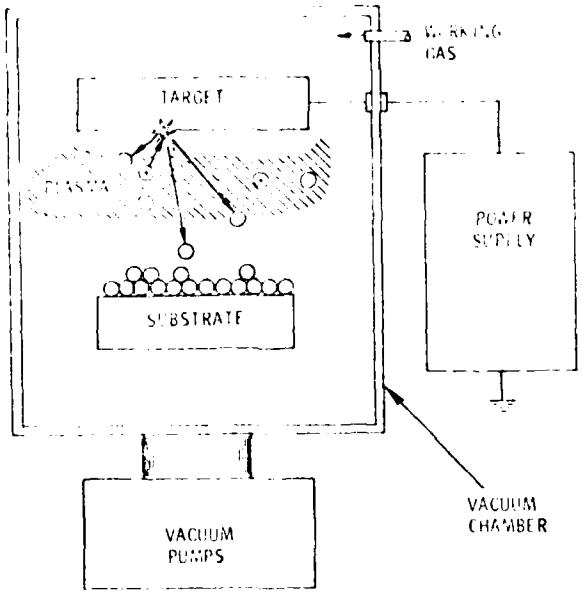



Figure 3. Basic sputtering process.

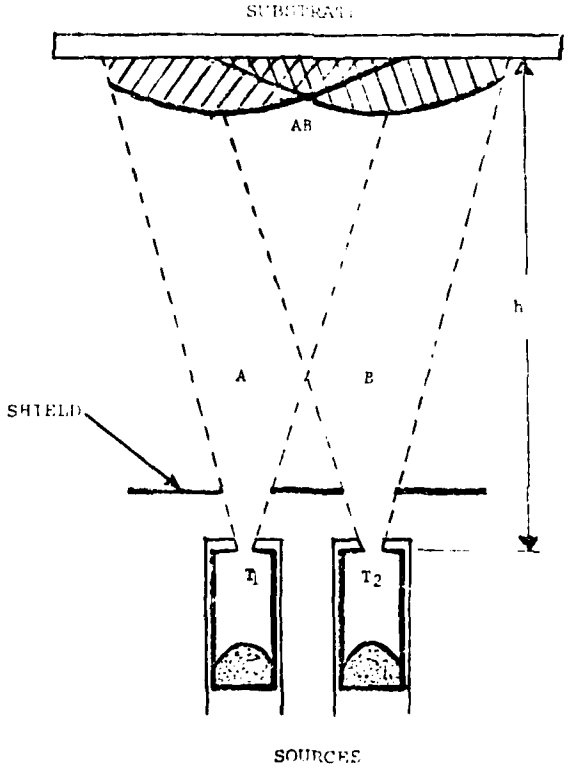



**Figure 4. Two source evaporation.**

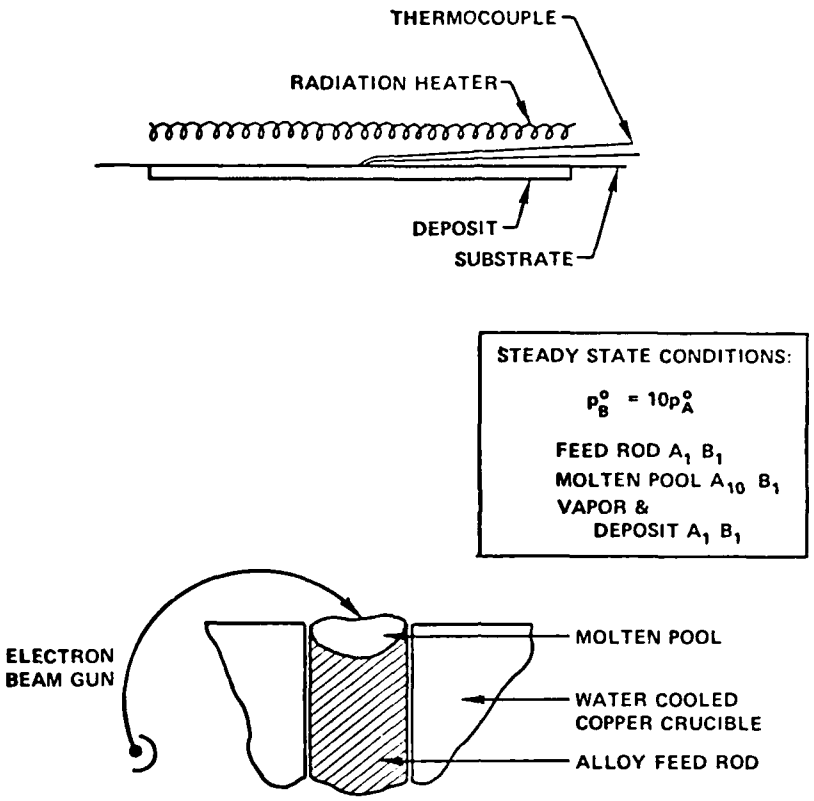



Figure 5. Alloy evaporation from a single rod fed source.

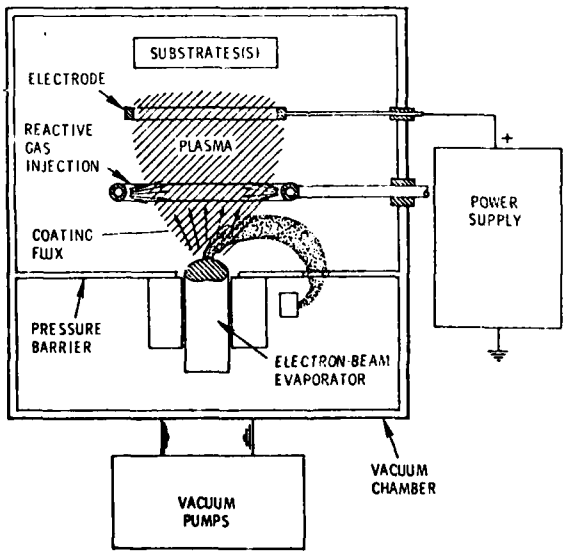



Figure 6. Activated reactive evaporation process.

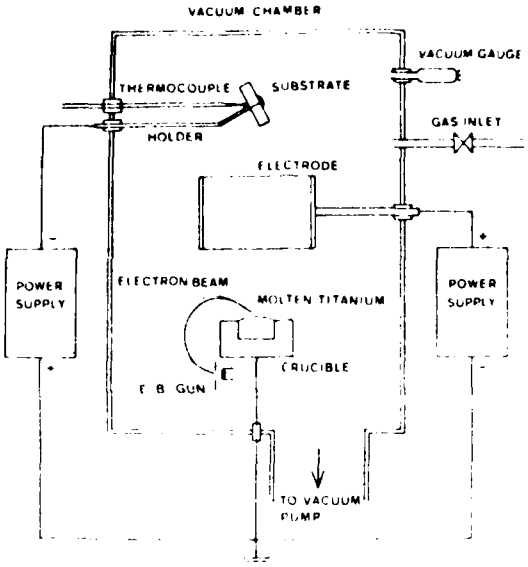



Figure 7. Reactive Ion Plating with auxillary electrode for low pressure operation in deposition of compounds. (Courtesy of Kobayashi & Doi [58]).

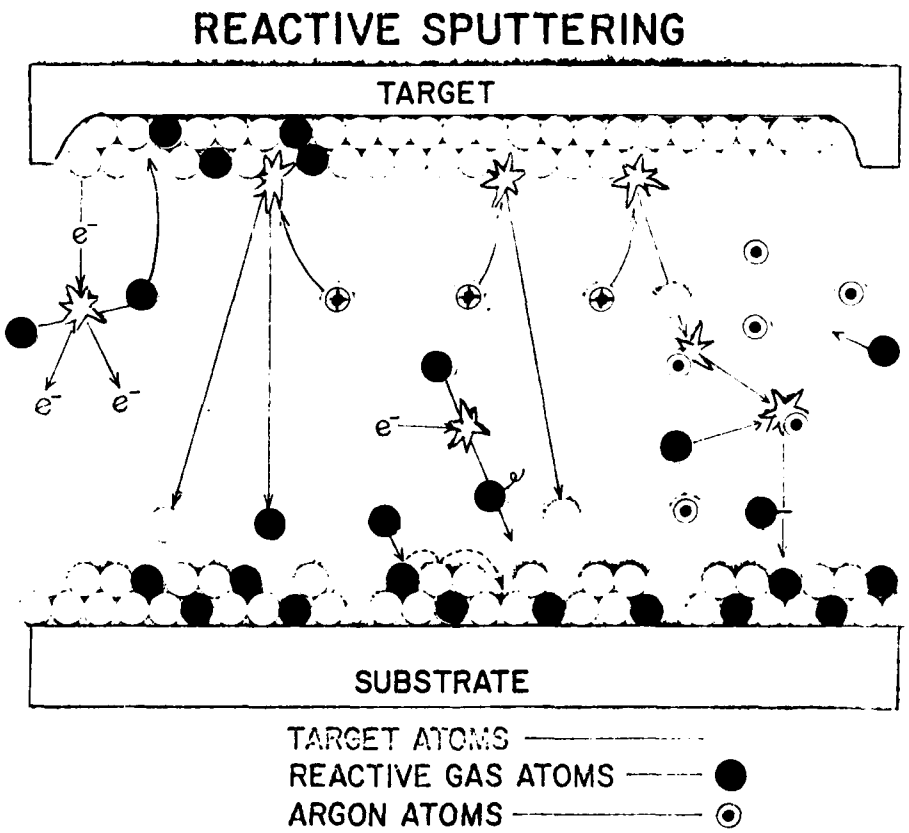
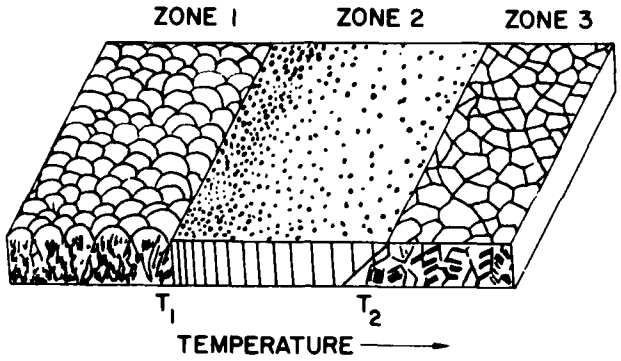



Figure 8. Reactive sputtering process. (Courtesy of Dr. John Thornton.)




| | ZONE 1 | ZONE 2 | ZONE 3 |
|---|---|---|---|
| METALS | $<0.3\ T'_m$ | $0.3 - 0.45\ T'_m$ | $>0.45\ T'_m$ |
| OXIDES | $<0.26\ T'_m$ | $0.26 - 0.45\ T'_m$ | $>0.45\ T'_m$ |

Figure 9. Structural Zones in Condensates at Various Substrate Temperatures. (Movchan and Demchishin)

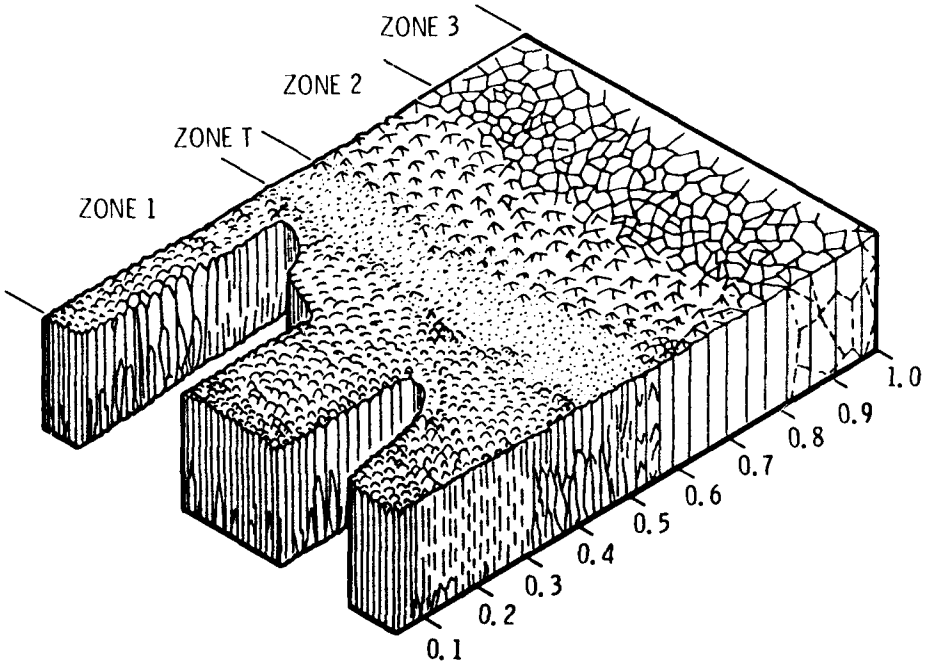



Figure 10, Structural zones in condensates showing the effect of gas pressure (Courtesy of Dr. John Thornton [69].)

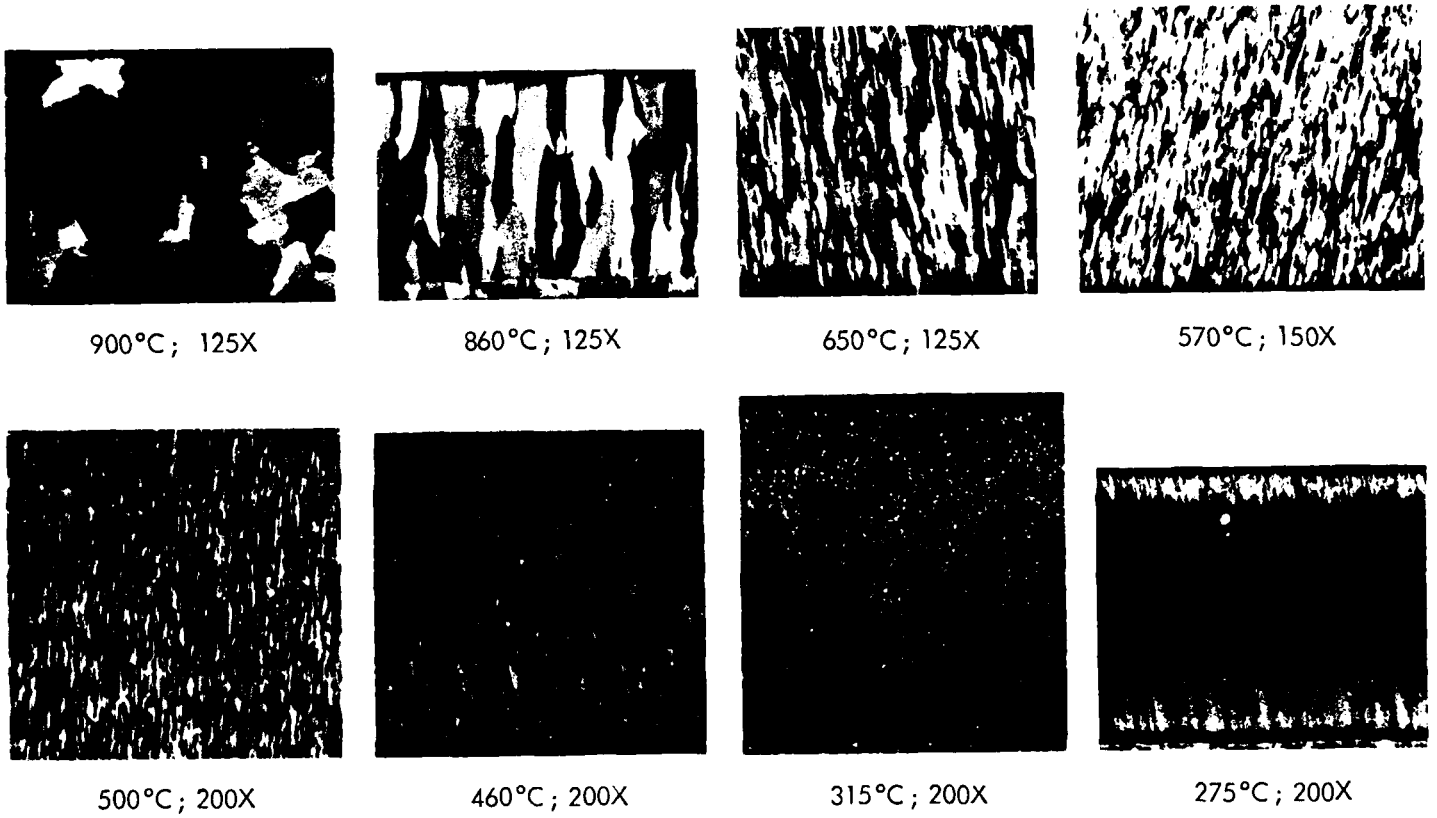



Figure 11. Structure of titanium deposits at various substrate temperatures. (Bunshah and Juntz [70].)

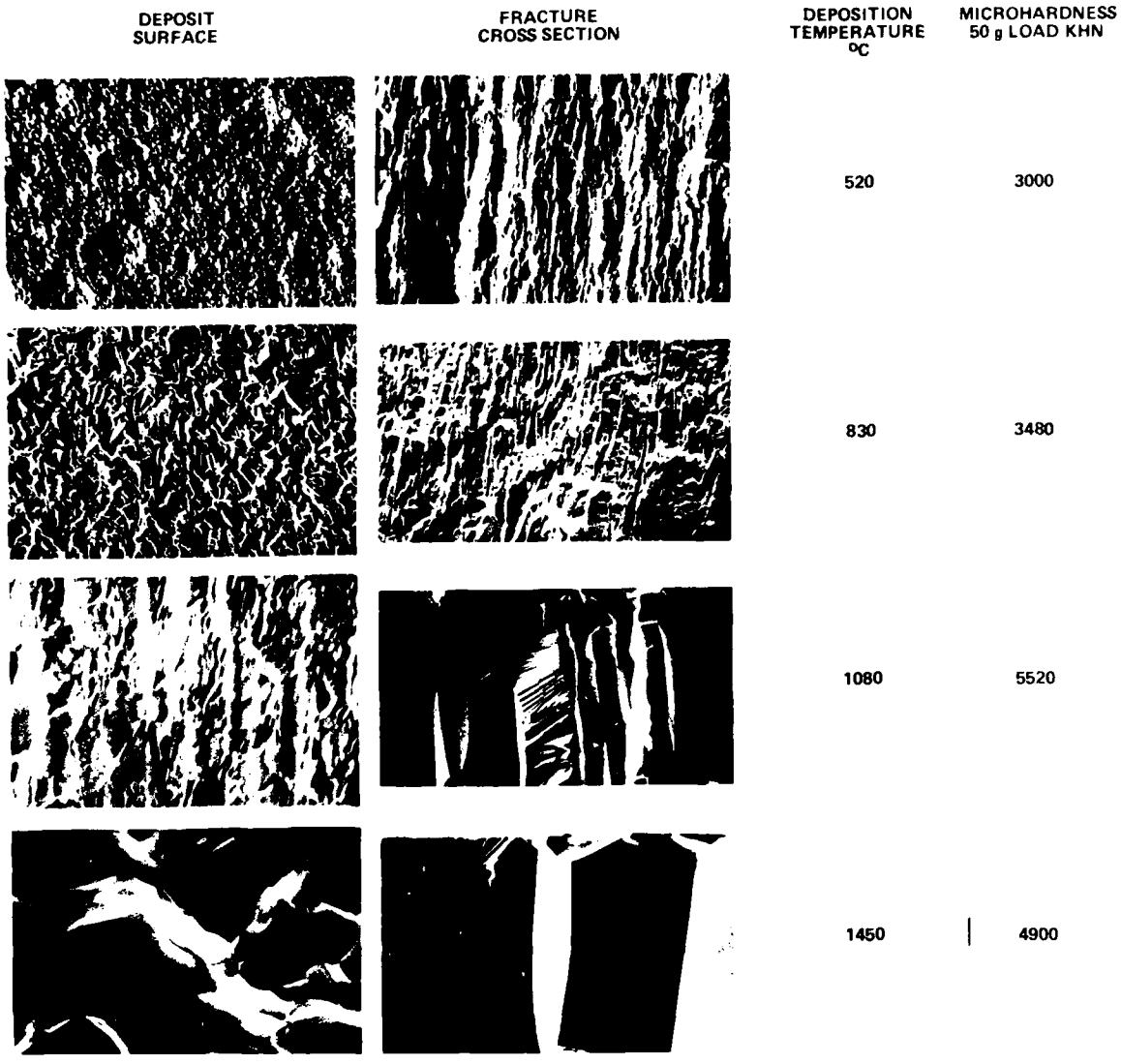



Figure 12. Structure of TiC deposits at various deposition temperatures. (Raghuram and Bunshah [79].)

# PLASMA AIDED TECHNIQUES

by

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## SUMMARY

The adhesion, crystallinity and grain structure of coatings deposited by Physical Vapour Deposition techniques are usually improved if the energy of the depositing particles is increased. Energy can be transferred to the coating atoms by heating the substrate. An alternative method is to increase the kinetic energy of deposition by ionising the vapour atoms and accelerating them in an electric field. A variety of Plasma Aided Techniques are described and it is shown that all the improvements brought about by high temperature substrates can be achieved at lower substrate temperatures. The very high ion energies can also cause production of unusual phases and a further advantage is the increased reactivity resulting in deposition of compound coatings.

## INTRODUCTION

For most applications of surface coatings, good adhesion between the coating and substrate is a prime requirement, and a dense, equi-axed (non columnar) grain structure is also desirable. It has been well known for many years that elevated substrate temperatures during deposition produce a number of advantageous effects. High temperatures aid surface diffusion, allowing the depositing species to find favoured sites, thus improving adhesion and structure. Also they promote diffusion across the interface, again improving adhesion and decreasing interfacial stresses. Substrate temperature is a critical parameter in determining the grain structure of the coating. Movchan and Demchishin have studied this effect in some detail and have proposed a three zone model for coating structures. If the substrate temperature is below about 0.3 Tm, where Tm is the melting point of the coating material in degrees Kelvin, then the coating has a structure (zone 1 structure) consiting of tapered columns and nodules with weak binding between adjacent columns. Between 0.3 Tm and 0.5 Tm the zone 2 structure is denser and consists of parallel columnar grains. At temperatures above about 0.5 Tm the coating has the properties of a fully annealed bulk material with equiaxed grains. The main conclusions have been confirmed by several investigators (2,3,4) and Thornton (5) has produced a modified model which includes the effect of gas pressure, in the range commonly used in sputtering, on the coating structures. Higher pressures tend to increase the substrate temperature necessary for the denser structures.

In 1963 Mattox introduced a technique of physical vapour deposition which he called "ion plating" (6). Mattox had compared the energies of deposition of sputtering, typically about 5eV, and vacuum evaporation, typically 0.2eV, and related these energies to the experimentally determined result that sputtered coatings were usually more adherent than vacuum evaporated coatings. He then attempted to increase the kinetic energy of the depositing atoms further by a glow discharge process, in order to further improve the adhesion. He was able to demonstrate that ion plated coatings had excellent adhesion and this was attributed to the high energy of deposition. Recent work (7,8) has shown that the energy due to ionisation effects in ion plating can modify and control the structure of the coating as does substrate temperature in the Movchan and Demchishin model. Thus we see that the energy of the depositing particles, whether imparted by substrate temperature or in the form of kinetic energy due to ionisation effects is an extremely critical factor in physical vapour deposition processes.

A further effect of using plasmas during coatings is the increased reactivity that can be realised during both reactive physical vapour deposition (4) and chemical vapour deposition (9). Bunshah has shown that it is extremely difficult to produce many compounds by reaction evaporation but when an intense plasma is formed as in Activated Reactive Evaporation (A.R.E.) a wide range of refractory metal carbides, nitrides and oxides can be deposited (4,10). Using Plasma Activated Vapour Deposition, Linger (9) has shown that the use of a plasma enables a significant reduction in substrate temperature to be made while depositing refractory metal carbides.

It is now generally accepted that plasmas can be used in place of substrate temperature in a wide range of deposition processes to improve coating adhesion and structure and to increase reactivity during reactive processes. As we shall see in the following paper this can be extremely important in a wide range of applications. However, it should be realised that plasma processes can produce very high "equivalent temperatures" in the depositing particles. For example, an ion which has passed through a potential of 100eV has an equivalent temperature of over $1 \times 10^6$ °K. This very high energy of deposition allows a new type of film deposition, not possible by conventional thermal or chemical means. As an example of this, a number of workers (11, 12, 13, 14) by using ion beam or plasma effects have produced carbon coatings, which are hard, and transparent, and exhibit many diamondlike characteristics.

In the following paper, ion plating and a range of plasma aided techniques are described. Their relative advantages and disadvantages, are discussed and some results and applications are included. It is beyond the scope of this paper to enter a detailed discussion of the mechanisms involved in the various processes but these are mentioned briefly together with references to the relevant literature.

ION PLATING

Ion plating is essentially physical vapour deposition in a soft vacuum on to a substrate which is held at a high negative potential, to form the cathode of a glow discharge. It is usual to sputter clean the substrate prior to deposition. The technique was first described by Berghaus (15) but it was the work of Mattox (6,16) that stimulated the considerable interest in, and the development of the process which has since taken place. Mattox, (16), Spalvins et al (17) and Chambers and Carmichael (18) have each given excellent descriptions of the apparatus. That shown in figure 1 is a basic equipment used by the author to study the technique and coatings. It contains all the essential features necessary for successful ion plating. The work chamber consists of a 300mm diameter glass chamber, 350mm high, sitting on a stainless steel base plate and with an aluminium alloy lid. The seals are neoprene "L" gaskets. The specimen or substrate is attached to an insulated H.T. electrode, mounted in the centre of the lid. The sample can be heated or cooled and the temperature is measured using a thermocouple, digital thermometer. The vapour is produced using resistance heating of a tungsten filament, or molybdenum boat, at earth potential. The pumping system is a conventional liquid nitrogen trapped, oil diffusion pump, rotary pump, combination. Argon gas can be admitted to the chamber in a controllable way by means of a needle valve. The pressure in the chamber is measured using an ionisation gauge, whose useful range has been extended to pressures as high as $10^{-1}$ torr, and that in the backing line by a thermocouple gauge. A 0-5 KV (negative), 500 mA D.C. supply heats the vapour source.

The plating procedure is as follows. The sample is connected to the H.T. electrode and a measured amount of coating material is placed in the filament (or boat). The chamber is evacuated to a pressure of $10^{-5}$ torr or better and then the baffle valve is partially closed and the needle valve opened in order to maintain a constant pressure of argon, typically between $10^{-2}$ and $5 \times 10^{-2}$ torr. The bias supply is adjusted to the required level, usually between 2 and 5 KV. Under these conditions an abnormal cold cathode glow discharge (19) is struck between the earthed parts of the apparatus and the sample (cathode). The sample is bombarded by the positive ions formed in the discharge, resulting in the removal of oxides and other contaminants from the surface. When the sample is sufficiently clean the vapour source is energised, the metal vapour enters the discharge, and is deposited on to the sample. When all the coating material has been evaporated the current to the vapour source, and the high voltage sample bias are switched off, and the plating process is complete.

The procedure as described here is rather limited in its application, but does contain all the essential features of ion plating. We will now consider methods used in practical plating systems.

PRACTICAL ION PLATING SYSTEMS

The ion plating system described above is not very convenient as a practical plating system. The resistance heated tungsten filament source limits the process in two ways. Only relatively low melting point materials can be evaporated and coatings of only a few microns in thickness can be deposited. Resistance heated crucibles with wire feed systems have been used to deposit thicker coatings of low melting point materials such as aluminium (20). Probably the most important advance in ion plating sources was that developed by Chambers and Carmichael (18) who, by using a double chamber construction and differential pumping were able to operate a hot filament electron beam gun at ion plating pressures. This type of system makes possible high deposition rates and evaporation of virtually all metals. The gun used was a 270° bent beam type (21). A similar system but with better beam scanning facilities has also been described (22,23) and is shown in Figure 2, as has an ion plating system using a Pierce type gun (24).

Cold cathode electron beam guns (25,26) have also been used in ion plating systems (27,28,29). These operate within the same range of pressures required by ion plating and therefore require little or no differential pumping. Two further types of source requiring no differential pumping and used in ion plating systems are induction heated sources (30,31) and sputter sources (32,33,34). In order to accomplish longer coating runs or thicker coatings from vapour sources it is necessary to use a feed system. The most commonly used type of feed systems are rod feed (35) or wire feed (20). Using such continuously fed systems it is possible to deposit alloys of controlled composition (36). Slug fed systems (37) can also be used and have advantages in those cases where it is difficult to obtain the relatively large rods required and where wires of the required alloy are too brittle to be used in wire feed systems. Recent work (38) has shown that close control of average alloy composition is easily achieved with slug feeds but that the coatings may have a layered structure.

In ion plating the sample to be coated is usually attached to the negative high voltage electrode. The exact design of the H.T. electrode/substrate holder depends on the size, shape and number of items to be coated. Holders for mass production coating of many small parts have been described (39,40), and Mattox and Bland (41) have reported an arrangement for obtaining a uniform coating over the surface of a complex part. One disadvantage of attaching samples to the electrode is that the part of the sample in contact with the electrode is not coated. An alternative method is to connect the negative high voltage to a rotating mesh cage in which the substrates are tumbled during deposition (42).

Insulating substrates can be coated by surrounding them by a wire mesh connected to the bias voltage (6, 43) but it is preferable to replace the D.C. bias voltage by an R.F. voltage (44) which prevents the build up of positive charge on the insulating surface.

R.F. bias on the samples has a further advantage. The ionisation efficiency obtained using R.F. is much greater than that from D.C. We shall see later that this can be of great importance for many applications. Also R.F. discharges are more stable than D.C. discharges for rough samples and they can be maintained at lower pressures than D.C. discharges.

Ionisation enhancement has been achieved by other methods. If a third electrode (sometimes called a probe) with a potential of about 100 volts positive is added to the usual ion plating system, the ion current density can be increased nearly tenfold (18,45). If this electrode is combined with a heated filament at earth potential, a hot cathode discharge (46) is the prime cause of ionisation, and the situation is similar to that used in a triode assisted sputtering system (47). This results in further

ionisation enhancement and the possibility of maintaining the discharge at pressures lower than $10^{-3}$ torr Enomoto and Matsubara (48) have successfully used hot filaments at the same potential as the substrates, to increase ionisation, and of course the hollow cathode electron beam gun (49), and magnetron sputter sources (50), both cause considerable increases in the discharge current in ion plating.

It should also be noted that the chamber, lid, baseplate, and any shields etc within the chamber, all act as electrodes in an ion plating system and large differences in results have been recorded between systems with earthed and floating components within the chamber (51).

In the above account of various systems, is included an ion plating system with a sputtering source. There are some important differences between such a system, usually called Sputter Ion Plating, and those with evaporation sources. Firstly, the sputter source operates at a much lower temperature than an electron beam gun and therefore there is much less radiant heat to the substrate. If the source is a magnetron system then ionisation enhancement occurs, and if it is an R.F. magnetron then deposition at low pressures are possible. Sputtering is inherently more stable than thermal evaporation, and constant deposition rates are easily achieved which can be important in reactive techniques. Controlled alloy deposition is also easy. The slower deposition rates can be a disadvantage, but as the ion current to the substrate, required to improve the coating structure is rate dependant, good structures can be achieved at lower ion currents (32). This, combined with low radiation is an advantage when temperature sensitive substrates are coated (34), a sputter ion plating system is shown in Figure 3.

ENERGIES OF DEPOSITING PARTICLES IN ION PLATING

In ion plating not all the vapour atoms are ionised in the discharge, and of those that are ionised few arrive with the full energy of the discharge (52). Measurements have shown that in the abnormal glow discharge normally used in ion plating, between 0.1% and 1% of atoms are ionised (52). Once an ion is formed it is accelerated across the cathode dark space, to the cathode (substrate). If an ion arrives at the substrate without colliding with other ions or neutrals it will have the full energy of the discharge, but at typical ion plating pressures of $10^{-2}$ torr the mean free path is about 5 mm, and therefore each ion has a high probability of undergoing several collisions before reaching the substrate, and in these collisions energy is lost to the colliding particle. Davis and Vanderslice (53) have reported the energy distribution of ions arriving at the cathode. They calculated that the number of ions arriving at the cathode with energy $e(V_c - V)$ is

$$dN = \frac{N_o L}{2\ell\sqrt{V_c V}} \exp - \frac{(L - L\sqrt{V/V_c})}{\ell} dV$$

where $V$ is an intermediate potential within the cathode dark space.

$V_c$ is the potential on the cathode.

$N_o$ is the number of ions leaving unit area of the negative glow per second.

$L$ is the length of the cathode dark space

$\ell$ is the mean free path

$e$ is the electronic charge.

It is easy to show by integrating this expression that the total energy carried by the ions approximates to $\frac{2\ell}{L} N_o V_c$ (52).

The total energy dissipated in the discharge is $N_o V_c$.

Under typical conditions $\frac{\ell}{L}$ is small, about $\frac{1}{20}$, which means that 10% of the energy is carried by ions, and 90% is carried by neutrals which have acquired energy in the collisions. These figures, arrived at initially, by calculations (52), based on the Davis and Vanderslice (53) theory, have been confirmed experimentally (43). They indicate that the beam energy of the particles, ions and neutrals, deposited by ion plating is usually not more than 100eV.

The ionisation efficiency and the mean energies of the depositing particles can both be increased by ionisation enhancement systems working at lower pressures as is described below.

ADHESION IN ION PLATING

The most important feature of ion plated coatings is the excellent adhesion, which is obtained even when the coating and substrate material do not alloy, and where diffusion is difficult. Mattox (54) has listed 19 different metal/metal combinations for which he reports excellent adhesion, and 5 metal on semi-conductor pairs where a wire, soldered to the metal and subsequently pulled caused failure in the solder and not at the interface. Spalvins (17) has also reported excellent adhesion for soft metal coatings on steel substrates, resulting in improved tribological properties as compared to vacuum-evaporated coatings. The author has subjected a wide variety of coating/substrate combinations to bend, tensile, shear and scratch tests, to thermal shock and to ultrasonic vibration. No failure of the adhesive bond has been recorded. Figure 4 shows steel tensile samples coated with silver, by ion plating and by vacuum deposition, which have been pulled to tensile failure. The ion plated coatings have remained adherent while the vacuum deposited coatings are detached over a large area. The excellent adhesion achieved by ion plating has been reported by many investigators and it can now be accepted as established fact. However the detailed reasons for the adhesion are far from clear. The adhesion has been associated with the formation of a graded interface between coating and substrate (54). Deep graded interfaces, i.e. greater than 1 micron have been reported for a number of combinations of coating and substrate materials where thermal diffusion is possible and it is probable that this is the major mechanism in these cases. However, in the case of incompatible pairs where conventional diffusion is difficult, the adhesion is still good, but is associated with a much shallower interface. In these cases the mechanism of interface formation is not clear. The average energies of argon and metal ions under typical ion plating conditions is about 100eV(52)

and this energy is insufficient to cause ion implantation to depths greater than a few atomic distances (57). Other available mechanisms include atomistic mixing of the species sputtered from the substrate with the depositing atoms, and recoil implantation (58). However it is probable that some form of ion aided or radiation induced diffusion (59) is responsible. What is beyond dispute is that the adhesion is associated with the high energy of deposition.

UNIFORMITY OF COATING

Unlike evaporation under a hard vacuum, ion plating can give good coverage on surfaces out of line of sight of the vapour source. Mattox (60), Spalvins et al (17) and Chambers and Carmichael (18) have given details of thickness distributions over hollow cylinders, bearings and various complicated shapes. Chambers and Carmichael (18) studied the throwing power in some detail, and reported the dependance of coating deposition rate on gas pressure for the front and back surfaces of a flat plate, and solid cylinder, and for the front, back and internal surfaces of a hollow tube. Their results for the flat plate were confirmed by Sherbiney (61) whose results are shown in Figure 5. This good throwing power exhibited by ion plating has been attributed to the ionised vapour atoms following the field lines to all parts of the sample. However, the ionisation efficiencies under typical ion plating conditions are less than 1%, (52), and ionisation effects can affect the throwing power only in a minor way. In fact, the work of Sherbiney (61) has indicated clearly that the throwing power can be attributed solely to gas scattering effects. Such gas scattering and throwing power can also be achieved by increasing the gas pressure during vacuum evaporation (62) but in this case the coating structure and adhesion is very poor. The high energy of deposition of ion plating counteracts the usual effects of high pressure (62) so that good adhesion, throwing power and structure can be achieved simultaneously.

GRAIN STRUCTURE IN ION PLATING

As reported earlier, the grain structure of coatings deposited by vacuum evaporation depend on the substrate temperature (1) as indicated in Figure 6 and also the gas pressure is an important parameter (5). The results are consistent with the observation that increased mobility of the depositing atoms improves the structure.

Ion bombardment during deposition has been shown to suppress the porous boundaries normally found in coatings formed at low substrate temperatures (63) and at higher temperatures ion bombardment causes grain refinement of beryllium coatings (64). The structures reported by Movchan and Demchishin (1) for vacuum evaporated coatings have been reported for ion plating by several authors (27, 7, 8, 65). In a systematic study Wan et al (27) found that coating structures deteriorated with increasing gas pressure in agreement with Thornton (5) but that increased substrate bias improved the structures, Lardon et al (7) deposited titanium and aluminium coatings by ion plating and found structures similar to those reported by Movchan and Demchishin (1). However, they found that the temperatures necessary to cause a change from zone 1 structure to zone 2, and zone 2 to zone 3, were reduced progressively as the substrate bias was increased. Similar results have been obtained by Teer and Delcea (8) for copper coatings as shown in Figure 7. Here it was found that the best structures were obtained at low pressures using a triode assisted discharge to increase the ionisation. One important difference between vacuum evaporated and ion plated coatings is that the dense zone 3 structures produced by ion plating are fine grained whereas they are large grained for vacuum deposition.

Many important results on the effect of ion bombardment during plating are being obtained using reactive ion plating. We will now consider this technique.

REACTIVE ION PLATING

If a reactive gas is added to or replaces the inert gas normally used in ion plating then the metal vapour can react with the gas and a compound coating is formed. For example, if titanium is evaporated into a discharge formed in nitrogen, then a titanium nitride coating can be deposited. This has some similarities to the Activated Reaction Evaporation technique (4), in which an intense glow discharge was found to be necessary for certain reactions. The same conclusion can be drawn for ion plating. Attempts to produce compound coatings by reactive ion plating have met with only limited success unless the intensity of ionisation was enhanced by some means. For instance Hill et al (66) found that high substrate temperatures were necessary for the formation of hard Ti N, and Stowell (68) deposited mixtures of unreacted titanium and carbon rather than titanium carbide. However many workers have reported successful coatings of compounds using reactive ion plating when the ionisation was increased by some means. Hollow cathode guns (68), induction heated sources (30), magnetron sputter sources (34), and triode assisted discharges (69) have all been used to enhance ionisation and to ion plate reactively. The results reported by Matthews and Teer (69) for titanium nitride deposition using a triode assisted discharge demonstrate the importance of ionisation enhancement. For a given titanium evaporation rate and nitrogen flow rate using only a diode discharge no reaction took place. As ionisation was increased $Ti_2$ N was formed and with further increase in ionisation Ti N was formed. Besides increasing the probability of reaction the enhanced discharge and resultant intense ion current to the substrate improve the coating structures, so that dense, equiaxed structures are formed at temperatures much lower than those required for C.V.D. (70). It is probable that the substrate ion current density required for dense structures increases with deposition rate (32). Using sputter ion plating with an R.F. bias on the sample, Ridge et al (34) have reported that the resistivity of the oxides of indium and inium-tin alloys were dependant on the discharge current. These coatings were deposited on heat sensitive plastic substrates without damaging the substrates. To obtain similar properties for coatings deposited without discharge required substrate temperatures in excess of 400°C (34, 71, 72).

ION PLATING - PROS AND CONS

Ion bombardment of the substrate prior to and during deposition leads to a number of advantages. These have been mentioned in the previous discussion but it is worthwhile listing them here. They include:

a) Good adhesion at low substrate temperatures.

b) Good coverage of complicated shapes (and other properties depending on structure

c) Improved structures at low substrate temperatures. at low substrate temperatures.

d) Enhanced reactivity.

The disadvantages of ion plating include:

a) The necessity of clamping the sample to a high voltage electrode.

b) The necessity of working in a relatively high gas pressure.

c) It is difficult to mask parts of the sample.

d) The energies of deposition cover a wide range and are difficult to determine or to control.

e) The technique is not suitable for coating internal surfaces of tubes.

A number of techniques have been developed recently which aim to exploit the advantages of the high energy of deposition of ion plating but avoiding some of the disadvantages. Some of these are now listed and brief descriptions given.

PLASMA AIDED CHEMICAL VAPOUR DEPOSITION

Chemical vapour deposition (70) is now a versatile technique for depositing many types of coating. It has a major advantage over P.V.D. techniques in that it is suitable for coating internal surfaces. However, for many applications it has an important disadvantage, that is, the requirement for high substrate temperatures. In Plasma Aided C.V.D. shown in Figure 8 an R.F. discharge is used to activate the reaction rather than high substrate temperature. Coatings of silicon nitride (73), silicon carbide (9) and carbon (74) have all been successfully deposited.

DEPOSITION BY ION SOURCES

Ion sources producing metal ions of close to mono-energetic distribution in the range 5eV to 100eV have been used in high vacuum deposition systems. Aisenberg and Chabot (12) used a beam of carbon ions and deposited coatings with diamondlike characteristics. Spencer et al (13) used a similar system, again obtaining diamondlike coatings. Other investigators (75, 76 ) have used ion beam source systems to investigate the effect of parameters on coating properties in a closely controlled manner. It is probable that this type of investigation into the relation between coating parameters and coating properties will be the main application of ion beam deposition systems in future. Even in those cases where the ion beam technique has produced unusual phases, such as diamondlike carbon, once the energy and other requirements for such phases have been elucidated, simpler and more practicable deposition systems can be devised (14, 74).

ION BEAM PLATING

Ion beam plating is the term used by Weismantel (14) to denote the technique of ionising and accelerating in the direction of the substrates a fraction of the atoms or molecules produced by a vapour source. Thus the deposition is by ions within a narrow energy band and thermal neutrals. The technique differs from ion plating in that deposition takes place in a good vacuum and the substrate is not electrically biased. Diamondlike carbon and chromium/carbon coatings with interesting properties have been deposited using this technique (14).

IONISED CLUSTER BEAM DEPOSITION

In ionised cluster beam deposition (77) a metal vapour expands adiabatically into a high vacuum region, and forms clusters containing between $10^2$ and $10^3$ atoms per cluster. These are ionised by an electron beam and accelerated through voltages up to 12 KV. The resultant coatings are adherent, crystalline and have desirable electrical properties. These properties together with the orientation of the coatings have been shown to be strongly dependent on the accelerating voltage (77). Thin film solar cells, electro-luminescent cells and ohmic contacts are some of the applications reported (77).

Clampitt et all (78) have reported a different type of ion source in which vapour from a molten pool is extracted and ionised by an intense electric field. This device can be used for ion beam deposition, but with an adjustment of parameters charged liquid droplets can be extracted and directed towards the substrate. This allows rapid deposition rates. Remarkable adhesion is reported and because of the rapid quenching of the liquid droplets, coatings can be "glassy".

DUAL BEAM DEPOSITION TECHNIQUES

There are now available a range of reliable inert gas ion sources (79, 80, 81, 82) and these are used to bombard the growing film. The source of vapour can be ion beam sputtering, or a thermal vapour source.

The dual beam sputtering system is yet a further technique where the energetics can be adjusted to produce diamondlike carbon coatings (14). It has also been used to produce silicon nitride reactively (14) in which case silicon was sputtered by an argon ion beam and the substrate was bombarded by a nitrogen ion beam. If the rate of sputter deposition is low, and the energies of the ions bombarding the substrate are high, then no film growth occurs, but the properties of the substrate can be modified by recoil implantation of the sputter deposited material (81).

When the film material is supplied by a thermal vapour source the technique has been called ion beam activated evaporation (14), or high vacuum ion plating (82). The main advantages of this technique over conventional ion plating are the close control over the energy of the bombarding particles and the high

vacuum (82). However, it should be remembered that with the use of ionisation enhancement, ion plating pressures can be lower than $10^{-3}$ torr. In fact, at the high deposition rates commonly used, the necessary vapour pressure can be provided solely by the metal vapour.

APPLICATIONS

Ion plated coatings and those deposited by other plasma aided techniques are finding increasing application in those cases where dense and adherent coatings are required and where substrate heating must be minimised. The even coverage over complicated surfaces can be an additional advantage and the fact that the technique is environmentally clean is becoming very important. A range of applications which exploit these characteristics is listed below.

LOW FRICTION COATINGS

Soft metal films on hard substrates are used in many applications where it is impossible to use conventional lubricants. The use of coatings in vacuum or space environments has been reviewed (83, 84, 85). In a wide range of coatings, applications and investigations ion plated coatings have been shown to have friction coefficients similar to coatings deposited by other techniques but to have much longer life times, due to the improved adhesion (17, 22, 61, 86, 87). Ion plated hexagonal close-packed metals have also been shown to have very low friction coefficients (88). A similar affect has been found after ion plating aluminium on titanium (55). The deep interface formed had a hexagonal close-packed structure and excellent frictional properties. Low frictions were also obtained from ion plated carbon coatings (45, 89) which had a highly crystalline structure.

WEAR RESISTANT COATINGS

The soft metal coatings on hard substrates used to provide low friction bearing surfaces in space applications also prevent the catastrophic adhesive wear usually associated with metallic rubbing contact in high vacuum (84). The aluminium-titanium interface (55) produced by ion plating also has good wear resistant properties. Heinz and Kienel (24) report ion plating nickel on A.B.S. or glass epoxy "golf ball" typewriter heads. The required lifetime was obtained with coating thicknesses only 10% of those deposited by a combination of electroless and electro-plating. White (30) describes the successful development of erosion resistant surfaces composed of ion plated refractory metal nitride and carbide layers, and also a tenfold increase of operating life of rotary engine parts due to ion plated coatings. The activated reaction evaporation technique (4) has been used to deposit a very wide range of wear resistant coatings. These show great promise as coatings for cutting tools (90) and in adhesive, abrasive and erosive wear tests (91). Similar coatings, again with good wear resistant properties have been deposited using reactive ion plating (24, 48, 49, 68, 69, 92, 93). These have been tested with excellent results in rubbing tests, cutting tool tests, and metal forming die tests. Plasma aided C.V.D. (9) also produces excellent wear resistant coatings of carbides and nitrides and of course the diamondlike carbon coatings (12, 13, 14, 74) must have application as wear resistant coatings.

CORROSION RESISTANT COATINGS

Mattox and Bland (41) have ion plated uranium fuel elements with aluminium 13 microns thick, for operation in an oxydising atmosphere at 150°C. No visible oxidation was detected after operation whereas electroplated nickel coatings spalled off under thermal shock.

Steel and titanium fasteners have long been protected by cadmium coatings. Cadmium is toxic and a substitute is sought (84). Ion plated aluminium (42, 55) is a successful alternative and production plant for coating many small items such as fasteners, and large items such as undercarriage components, has been in use for a number of years. Work is proceeding to improve the galvanic action of such coatings by developing methods for depositing aluminium alloys (38).

The structures of alloy overlay coatings for gas turbine blades can be improved without post deposition treatment by using plasma aided techniques (95) and ion plating is reported to improve coating uniformity without degradation of structure due to the presence of the inert gas (96).

Iron chromium films deposited by ion plating are found to exhibit high resistance to pitting corrosion in aqueous salt solution (97), and platinum coatings on titanium increase the oxidation resistance substantially while improving the high temperature fatigue strength (98).

DECORATIVE COATINGS

The automotive industry is increasingly requiring metal coatings on plastic parts to replace components traditionally made from metal and often with an electroplated finish. P.V.D. techniques are used and plasma aided P.V.D. is particularly suitable because of the adhesion and uniformity of the coatings (101). A novel application is the ion plating of titanium nitride, which is gold coloured on to watch cases to replace conventional gold coatings with a coating that is decorative, and both corrosion and wear resistant (48, 93).

OPTICAL COATINGS

The deposition of coatings for optical components has been recently reviewed by MacLeod (101). Ridge et al (34) report excellent properties from transparent oxides of indium and indium-tin alloys deposited by reactive ion plating. Zinc sulphide coatings deposited by ion plating have excellent humidity resistance (102) and if the ionisation is enhanced during deposition the abrasion resistance is also good (103). Laser mirrors are produced by ion plating gold on glass or quartz (104) and abrasion resistant transparent coatings of oxides of silicon and titanium are readily ion plated on to plastics at low temperatures (105).

## ELECTRICAL COATINGS

Ion plated metal coatings have found wide spread use as electrical contacts (106). Heinz and Kienel (24) describe improvements due to using noble metal ion plated coatings on reed blade contacts and report that such coatings are in large scale production. Hinoul (107) used ruthenium coatings for similar applications. Takagi et al (77) have described a number of applications of coatings deposited by ion beam techniques.

## MISCELLANEOUS APPLICATIONS

An extremely important application for ion plated coatings is as a "strike plate" for subsequent electroplating of difficult materials (106). For example Stupp describes the successful electro-deposition of 500 microns of Copper on titanium, with an intermediate layer of 2.5 microns of ion plated copper. Copper can be ion plated on aluminium conductors to facilitate soldering, (106) and metals such as aluminium alloys, titanium alloys, magnesium alloys, can be self brazed by ion plating the two mating surfaces with silver and holding the two parts together at 580°C in an inert atmosphere (106). The author has ion plated aluminium on stainless steel which was then welded to bulk aluminium. When the joint was pulled to tensile failure it parted in the weld metal and not at the interface. High strength ceramic-metal seals have been produced by ion plating (109).

White ( 30 ) reports using ion plating to refurbish worn components, such as pistons in aircraft engines, by depositing sufficiently thick coatings. Targets to produce soft X-rays are produced by ion plating metals such as aluminium and magnesium on copper (22). The production of heavy ions from electrostatic accelerators requires the use of self supported carbon stripper foils. The most usual method of producing such foils is by vacuum evaporation. However, much improved foil lifetimes are obtained if they are deposited either by ion plating (110) or by the cracking of a hydrocarbon gas by means of a plasma (111). The increased lifetimes are probably due to the improved structures associated with the high energy of deposition.

## CONCLUSIONS

The term, plasma aided techniques now covers a variety of coating systems, in which high ion energies are used to improve coating adhesion, to modify the structure and to increase chemical reactivity. The exact mechanisms involved are not yet fully understood but the dependance on energy has been amply demonstrated. Pure metal, alloy and compound coatings can be deposited on most substrate materials and because of their flexibility, plasma aided techniques are being increasingly employed to deposit a wide range of coatings in an equally wide range of applications.

1. B A Movchan and A V Demchishin, Fiz. Metall. Metalloved 28, 653, 1969.

2. J A Thornton, J. Vac. Sci. Technol., 12, 830, 1975.

3. A C Raghuram and R F Bunshah, J. Vac. Sci. Technol., 9, 1389, 1972.

4. R F Bunshah, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June 1977. CEP Consultants, Edinburgh, p. 207.

5. J A Thornton, Ann. Rev. Mater. Sci., 7, 239, 1977.

6. D M Mattox, J. Appl. Phys., 34, 2493, 1963.

7. D G Teer and B L Delcea, Thin Solid Films, 54, 295, 1978.

8. M. Lardon, R. Buhl, H. Signer, H K Pulker and E Moll, Thin Solid Films, 54, 317, 1978.

9. K R Linger, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June 1977, C.E.P. Consultants, Edinburgh, 1977.

10. R F Bunshah and A C Raghuram, J. Vac. Sci. Technol., 9, 1385, 1972.

11. S Aisenberg and R W Chabot, J. Appl. Phys., 42, 2953, 1971.

12. S Aisenberg and R W Chabot, J. Vac. Sci. Technol, 10, 104, 1973.

13. E G Spencer, P H Schmidt, D C Joy and F J Sansalone, Appl. Phys. Letters, 29, 118, 1976.

14. C Weissmantel, K Bewilogua, H J Erler and G Reisse, Proc. Conf. Ion Plating and Allied Techniques, London, July 1979. C.E.P. Consultants, Edinburgh, 1977, p 272.

15. B Berghaus, U.K. Patent Specification, 510, 993, 1938.

16. D M Mattox, J. Vac. Sci. Technol, 10, 47, 1973.

17. T Spalvins, J.S. Przybyszewski and D H Buckley, NASA, TND-3707, 1966.

18. D L Chambers and D C Carmichael, Research/Development, 22, 32, 1971.

19. J R Acton and J D Swift, 'Cold Cathode Discharge Tubes', London, Heywood, 1963.

20. E R Fannin and K E Steube, 'Triservice Corrosion of Military Equipment', Conference, Dayton, Ohio, October 1974.

21. C W Hanks, J D Mervill and H A Peterson, U.S. Patent, 3, 420, 977, 1969.

22. D G Teer, Tribology International, 8, 247, 1975.

23. D G Teer, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June 1977. C.E.P. Consultants, Edinburgh, 1977, p 13.

24. B Heinz and G Kienel, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June 1977. C.E.P. Consultants Edinburgh, 1977 p. 73.

25. J R Morley and H R Smith, J. Vac. Sci. Technol, 9, 1377, 1972.

26. R A Dugdale "Glow Discharge Materials Processing", London, Mills and Boone, 1971.

27. C T Wan, D L Chambers and D C Carmichael, J. VAc. Sci. Technol, 8, 99, 1971.

28. P S McLeod and G Mah, J. Vac. Sci. Technol, 11, 119, 1974.

29. D G Williams, J. Vac. Sci. Technol, 11, 374, 1974.

30. G W White, Research/Development, 24, 43, 1973.

31. T Spalvins and W A Brainard, NASA Tm X-3330, January 1976.

32. R A Dugdale Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June 1977, C.E.P. Consultants, Edinburgh, 1977, p 177.

33. S Schiller, U Heisig and K Goldicke, Proc. 7th Int. Vac. Congr. Vienna, 1977, p 1545.

34. M I Ridge, R P Howson, J N Avaritsiotis and C A Bishop, Proc. Conf. Ion Plating and Allied Techniques London, July 1979. C.E.P. Consultants, Edinburgh 1979, p 21.

35. K Kennedy, U.S. Patent, 3, 607, 222, 1969.

36. H R Harker and R J Hill, J. Vac. Sci. Technol, 9, 1395, 1972.

37. K B Cross and J O'Donnell, Vacuum, 29, 9, 1979.

38. D G Teer and O Abu Zeid. To be presented at Int. Conf. Metal Coatings. San Diego, April 1980.

39. R F Janninck, C R Heiden and A E Guttensohn, J. Vac. Sci. Technol, 11, 535, 1974.

40. J Starkovich, Sandia Corp. Report, SC-DR-68-188, 1968.

41. D M Mattox and R D Bland, J. Nucl. Mats., 21, 349, 1967.

42. K E Stenbe and L E McCrary, J. Vac. Sci. Technol, 11, 362, 1974.

43. D G Teer, B L Delcea and A J Kirkham, J. Adhesion, 8, 171, 1976.

44. J G Davy and J J Hanak, J. Vac.Sci. Technol., 11, 43, 1974.

45. M Salama, Ph.D. Thesis, University of Salford, 1979.

46. P Parker, "Electronics", E. Arnold, London 1955.

47. T C Tisone and P D Cruzan, J. Vac. Sci. Technol, 12, 1058, 1975.

48. Y Enomoto and K Matsubara, J. Vac. Sci. Technol., 12, 827, 1975.

49. S Komiya and K Tsurnoka, Proc. 6th International Vac. Congress, March 1974, Kyoto, p 415.

50. S Schiller, U. Heisig, K Steinfelder and K Gehm, Proc. 2nd Int. Conf. Metal Coatings, San Francisco 1977

51. D G Teer, B Kirkham and A J Kirkham, Proc. Ion Plating and Allied Techniques Conf., London July 1979. C.E.P. Consultants, Edinburgh 1979 p 35.

52. D G Teer. J. Adhesion, 8, 289, 1977.

53. W D Davis and T A Vanderslice, Phys. Rev. 131, 319, 1963.

54. D M Mattox, Sandia Corporation Monograph, SC-R-65-852, 1965.

55. D G Teer and F Salem, Thin Solid Films, 45, 583, 1977.

56. J M Walls, D D Hall, D G Teer and B L Delcea, Thin Solid Films, 54, 303, 1978.

57. G Carter and J S Colligon, "The Ion Bombardment of Solids", W Heinemann, London 1968.

58. R S Nelson, Proc. Conf. Ion Plating and Allied Technologies, Edinburgh June 1977. C.E.P. Consultants, Edinburgh, 1977.

59. J V Sharp, AERE Report No. R.6267, 1969.

60. D M Mattox, Trans. SAE. 2175, 1969.

61. M G El Sherbiney, Ph.D. Thesis, University of Salford, 1975.

62. K D Kennedy, G R Schenermann and H R Smith, Research/Development, 22, 40, 1971.

63. D M Mattox and G J Kominiak, J Vac. Sci. Technol 9, 528, 1972.

64. R F Bunshah and R S Juntz, J. Vac. Sci. Technol, 9, 1404, 1972.

65. P A Higham and D G Teer, Thin Solid Films, 58, 121, 1979.

66. R J Hill, G Schenermann and R Lucariello, Thin Solid Films, 40, 217, 1977.

67. W R Stowell, Thin Solid Films, 22, 111, 1974.

68. T Sato, M Tada, Y C Huang and H Takei, Thin Solid Films, 54, 61, 1978.

69. A Matthews and D G Teer, Proc. Conf. Ion Plating and Allied Techniques, London, July 1979, CEP Consultants, Edinburgh, 1979.

70. A J Perry and N J Archer, AGARD Lecture Series No 106, Materials Coating Techniques, 1980.

71. J C Fan, F J Bachner and C H Filey, Appl. Phys. Letters, 31, 773, 1977.

72. C E Wickersham and J R Gran, Phys. Stat. Solidi, 47, 329, 1978.

73. B Bourdon and G Sifre, Proc. 5th Int. Conf. C.V.D. Fulmer, Bucks, U.K. Sept. 1975, p 281.

74. L Holland and S M Ojha, Thin Solid Films, 38, L17 1976.

75. J H Freeman, W Temple, D Beanland and G A Gard, Nucl. Instrum. Methods, 135, 1 1976.

76. J Amano and R P Lawson, J Vac. Sci. Technol, 14, 831, 1977.

77. T Takagi, I Jama and A Sasaki, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June 1977. C.E.P. Consultants, Edinburgh, 1977.

78. R Clampitt, L Gowland and K L Aitken, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June 1977. C.E.P. Consultants, Edinburgh, 1977.

79. A H McIlraith, J. Vac. Sci. Technol., 9, 209, 1972.

80. J Franks and A M Ghander, Vacuum, 24, 489, 1974.

81. G Fischer, A E Hill and J S Colligon, Vacuum, 28, 277, 1978

82. J Franks, Proc. Conf. Ion Plating and Allied Techniques, London, July 1979. C.E.P. Consultants, Edinburgh, 1979, p 55.

83. E E Bisson, NASA SP-38 1964.

84. D H Buckley, NASA, SP-277, 1971

85. D G Teer and J H Halling, Annals CIRP 27, 517, 1978.

86. D W Wisander, NASA TN-D-64555 1971

87. N Ohmai, J. Vac. Sci. Technol, 13, 82, 1976.

88. D G Teer and R D Arnell, U.K. Patent Application 35448/74, 1974.

89. D G Teer and M Salama, Thin Solid Films, 45, 1977.

90. R F Bunshah, A H Shabaik, R Nimmagadda and J Covy, Thin Solid Films, 45, 453, 1977.

91. R F Bunshah and A K Suri, Proc. Conf. Ion Plating and Allied Techniques, London July 1979. C.E.P. Consultants, Edinburgh, 1979, p 230.

92. K Nakamura, K Inagawa, K Tsuruoka and S Komiya, Thin Solid Films, 40, 155, 1977.

93. B Zega, M Kornmann and J Amignet, Thin Solid Films, 45, 517, 1977.

94. R Suchentrunk, AGARD Lecture Series No 106, Materials Coating Techniques, 1980.

95. R A Burt, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh June 1977. C.E.P. Consultants, Edinburgh, 1977, p 135.

96. D H Boone, D Lee and J M Shafer, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June, 1977. C.E.P. Consultants, Edinburgh 1977, p 141.

97. W B Nowak and B A Okovie, Proc Conf. Ion Plating and Allied Techniques, London, July 1979. C.E.P. Consultants, Edinburgh, 1979, p 153.

98. T A Eckler, B A Manty and S Fujishiro, Proc Conf. Ion Plating and Allied Techniques, London, July 1979. C.E.P. Consultants, Edinburgh 1979, p 128.

99. D M Lindsey, Products Finishing. 32, 34, 1979.

100. R I Sims, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June 1977. C.E.P. Consultants, Edinburgh, 1977, p 86.

101. H A MacLeod, Proc. Conf. Ion Plating and Allied Techniques, London July 1979. C.E.P. Consultants, Edinburgh, 1979, p 74.

102. E Henderson, Proc. Conf. Ion Plating and Allied Techniques, Edinburgh, June 1977. C.E.P. Consultants, Edinburgh, 1977, p 122.

103. I M Reid, H A MacLeod, E Henderson and M J Carter, Proc. Conf. Ion Plating and Allied Techniques, London, July 1979. C.E.P. Consultants, Edinburgh, 1979, p 114.

104. B Raicu and G Dinca, Proc. Conf. Ion Plating and Allied Techniques, London, July 1979. C.E.P. Consultants, Edinburgh, 1979, p 99.

105. J N Avaritsiotis and R P Howson, Proc. Conf. Ion Plating and Allied Techniques, London, July, 1979. C.E.P. Consultants, Edinburgh, 1979, p 103.

106. R I Sims, Metallurgist Mats. Technologist, 10, 21, 1976.

107. M Hinoul, Thin Solid Films, 45, 539, 1977.

108. T Takagi, I Yamada and A Sasaki, Proc. Int. Conf. Low Energy Ion Beams, Salford, September 1977. Inst. of Physics, 1978, p 142 and p 229.

109. R Cuthbertson and D M Mattox, Proc 8th Conf. Tube Techniques. I.E.E.E. New York, 1966, p 101.

110. D W L Tolfree, D G Teer and M Salama, Proc. Conf. Ion Plating and Allied Techniques, London, July 1979. C.E.P. Consultants, Edinburgh, 1979, p 144.

111. D S Whitmell and R Williamson, Thin Solid Films, 35, 255, 1976.

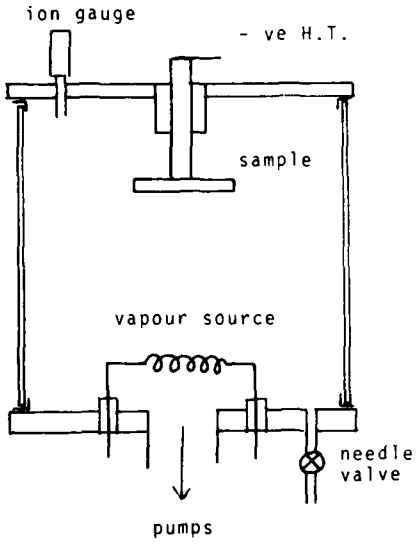


FIGURE 1. BASIC ION PLATING RIG

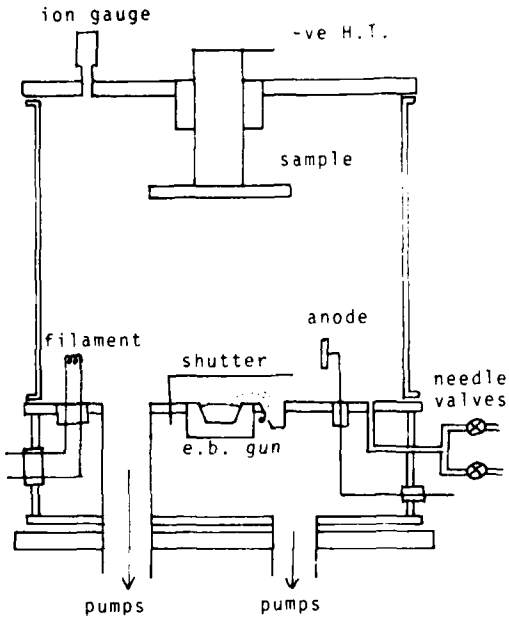


FIGURE 2. ELECTRON BEAM GUN ION PLATING RIG

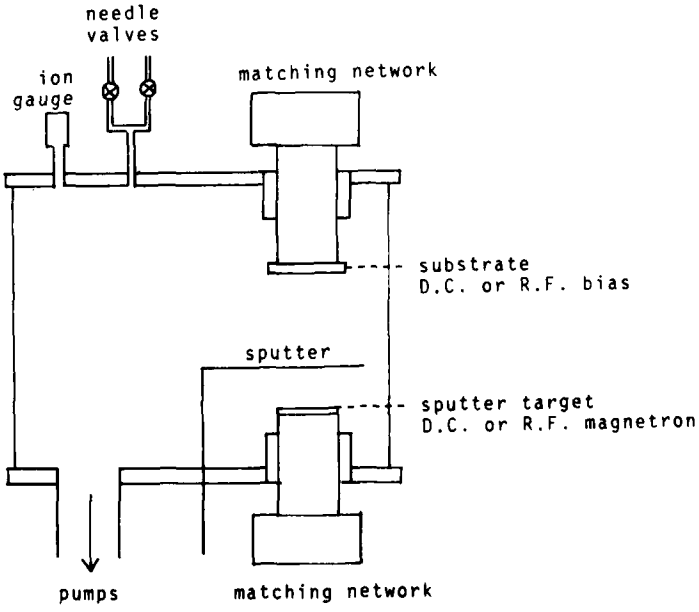


FIGURE 3. SPUTTER ION PLATING RIG

FIGURE 4. SILVER PLATED STEEL TENSILE SPECIMENS
Those on left were vacuum evaporated, those on right ion plated.

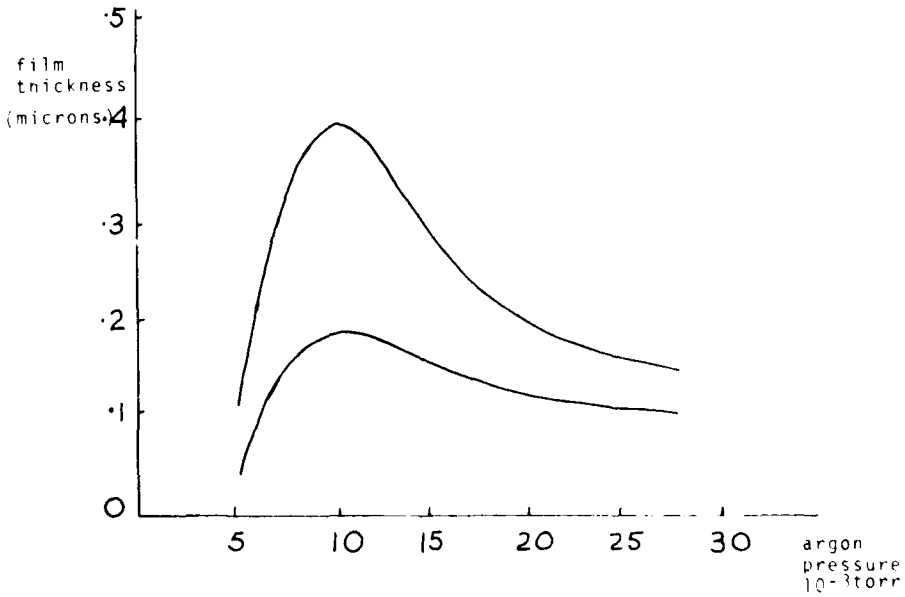


FIGURE 5. FILM THICKNESS AS FUNCTION OF ARGON GAS PRESSURE.[61]

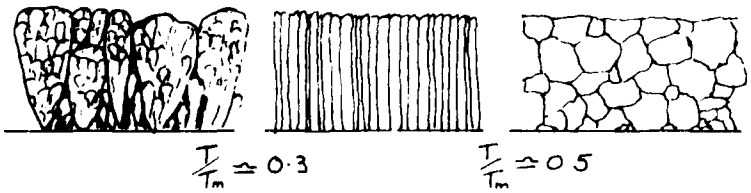


FIGURE 6. STRUCTURAL ZONE MODEL[1]


FIGURE 7. ION PLATED COPPER SAMPLES(FRACTURE SECTIONS)

a Low power ion plating Columnar zone 1 structure.

b Zone 3 structure produced by ionisation enhancement.

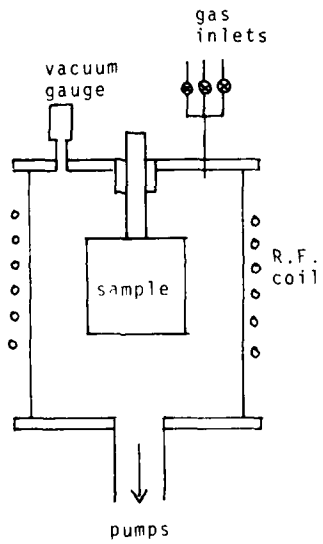


FIGURE 8. PLASMA AIDED C.V.D.

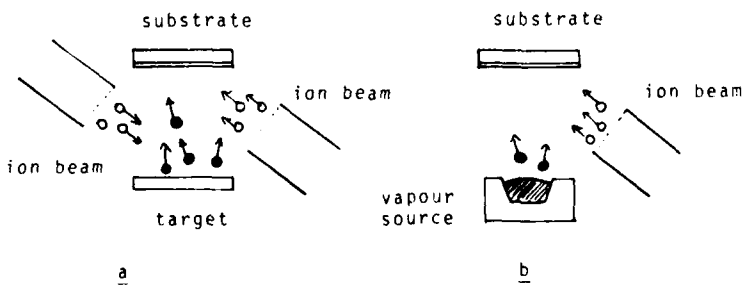


FIGURE 9. a DUAL BEAM SPUTTER DEPOSITION
b HIGH VACUUM ION PLATING

# TECHNIQUES OF CHEMICAL VAPOUR DEPOSITION

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## ABSTRACT

The technique of chemical vapour deposition utilises gas phase chemical reactions to produce a wide range of metallic and ceramic coatings. The technique is used to form very thin layers of refractory carbides (e.g. TiC) for wear resistance, layers of metals (e.g. Ta) for corrosion and oxidation resistance, but it is also a forming technique which permits the fabrication of complex shapes, particularly in high temperature materials (e.g. pyrolytic graphite).

Chemical vapour deposition depends upon a localised chemical reaction and so it is able to coat complex shapes, particularly internal surfaces. However, the reactions currently used for chemical vapour deposition often require high reaction temperatures (>500°C) and this causes many limitations in terms of the substrates which may be coated.

This paper reviews the basic technique of chemical vapour deposition, the equipment used, and the properties of the materials produced.

## 1. INTRODUCTION

Chemical vapour deposition produces a thin solid coating on a heated substrate by means of a chemical reaction between gaseous reactants passing over the substrate. Reaction temperatures can be anywhere between about 200°C and 2200°C, but are mostly between 500-1100°C. The actual optimum for a given reaction often lies within a very narrow range so that the whole process needs to be tailored to the substrate and to the intended application. The substrate melting point and its susceptibility to chemical attack by the reacting gases or by their side-products needs to be considered. So too does the intended application as this indicates which properties are most significant: thickness, smoothness, freedom from porosity, microstructure, colour etc. Coatings find application in a wide array of corrosion and wear resistant uses, but also decorative layers, semiconductors, magnetic and optical films can be produced.

Possibly the simplest chemical reaction is the breakdown of some compounds which occurs on heating. Compounds such as carbonyls and iodides are often stable at low temperature but "crack" when passed over a suitably heated substrate:

$$Ni(CO)_4 \rightarrow Ni + 4\ CO \qquad - 1$$

This is the basis of the Mond process (1) for nickel where the CO gas can be recirculated to create a cyclic process and more recently it has been used to 'vapour form' plastics moulds in nickel. The van Arkel - de Boer process (2) for producing tungsten for electric light bulbs and the current industrial iodide process for refining titanium and zirconium operate in the same way.

Hydrogen reduction of a volatile compound is much more usual. An example (Figure 1) is:-

$$TaCl_5 + 5/2\ H_2 \rightarrow Ta + 5\ HCl \qquad - 2$$

whereby a metallic coating of tantalum is produced at 900-1000°C with application where corrosion resistance in chemical environments is required[3]. Mutual reduction can also be used:

$$WF_6 + C_6H_6 + H_2 \rightarrow W_2C + HF \qquad - 3$$

to produce a wear resistant carbide coating on steel tools at about 500°C[4].

There are many such reactions which can be used to produce carbides, nitrides and oxides[5].

$$SiCl_4 + CH_4 \rightarrow SiC + HCl \qquad -4$$

$$SiCl_4 + NH_3 \rightarrow Si_3N_4 + HCl \qquad -5$$

$$BCl_3 + CH_4 \rightarrow B_4C + HCl \qquad -6$$

$$AlCl_3 + CO_2 + H_2 \rightarrow Al_2O_3 + HCl + CO \qquad -8$$

It is possible to distinguish between three conceptually different types of surface treatment. The first type is that where an alement is allowed to diffuse into the surface to make an alloy with the substrate in the form of a diffusion profile;

examples of such profiles are chromizing and manganizing. The second is the growth of a chemically distinct layer on the substrate as in the case of the tungsten carbide reaction quoted above. A sub-group exists where a substrate is chosen which has no adherence with the coating, allowing its subsequent removal to form a free-standing body. The third is a combination of growth and diffusion where, for example, chromium is deposited on to the substrate and reacts with carbon drawn from the steel to form a carbide layer: other examples include nitriding and boronizing where the substrate takes part in the reaction to form nitrides or borides.

In this article examples of the different types of coating are given. These have been chosen to give an indication of the wide range of treatment temperatures, substrates and applications which are open to chemical vapour deposition.

## 2. SOME THERMODYNAMIC CONSIDERATIONS

When CVD is carried out by reducing a volatile compound with hydrogen, then the compound should be sufficiently stable thermally to be transported and yet readily reduced with hydrogen at a temperature consistent with usual technology (i.e. in general not above some 1200°C). From a practical point of view it is very useful if the compound is volatile at ambient temperature, although heated reactant generators are often used.

The most frequently used compounds are chlorides. Free energy curves (6,7) of the type shown in Fig. 2. indicate which compounds can be reduced; the free energy of formation, $\Delta G$, per mole of chloride is plotted in the figure to permit the comparison with HCl. As examples, both $MoCl_5$ and $TaCl_5$ can be reduced following the reaction

$$MoCl_5 + 5/2\ H_2 \rightarrow Mo + 5\ HCl \qquad - 9$$

and reaction 2 respectively, because the HCl formed is a more stable chloride, chemical stability increasing when descending scale of the free energy of formation. As a further example, it is apparent from Fig. 2. that $CrCl_2$ does not intersect the HCl curve. It can be made to do so by adjusting the partial pressures in the system, keeping that of HCl low and that of $H_2$ high.

Taking the gas partial pressures into account, the free energy of the reaction:

$$CrCl_2 + H_2 \rightarrow Cr + 2\ HCl \qquad - 11$$

is given by

$$\Delta G = \Delta G^o + RT \ln \frac{P^2_{HCl}}{P_{H_2}} \qquad - 12$$

assuming both $CrCl_2$ and Cr to be solid. At 800°C and setting $\Delta G = 0$ for the equilibrium condition (3):

$$\Delta G^o = - RT \ln \frac{P^2_{HCl}}{P_{H_2}} = - 14.8 \text{ kcal.} \qquad - 13$$

With a total pressure of 1 atm, the partial pressures are $p_{HCl} = 0.031$ atm and $p_{H_2} = 0.969$ atm so that chromizing will occur as long as the partial pressure of HCl is held below 3.1% and free hydrogen is continuously introduced. In general this type of consideration allows any chloride which lies within some 26 Kcal of $\Delta G_{HCl}$ to be reduced with hydrogen.

Fluorides are more stable than chlorides and none decomposes thermally. Only the refractory metals such as tungsten, molybdenum and rhenium can be reduced from their fluorides with hydrogen.

Iodides and bromides are seldom used in CVD apart from the refining of titanium and zirconium mentioned above when the thermal stability is specifically exploited.

Such thermodynamic considerations can be applied to other CVD reactions including, for example, carbide formation (8).

$$TiCl_4 + CH_4 \rightarrow TiC + HCl \qquad - 10$$

In this case the behaviour at all temperatures can be evaluated by comparing ($\Delta G^o$chloride - $\Delta G^o$HCl), from the chloride diagram, with ($\Delta G^o$ carbide - $\Delta G^o CH_4$) from the carbide diagram.

In just a few CVD reactions the starting materials are actually thermodynamically unstable even at the temperatures under which they are normally stored. The kinetic barriers to their decomposition are sufficient to stop the process at ambient temperature, but on passing into a heated chamber the decomposition can proceed. Examples, based on this principle, are the formation of aluminium from aluminium alkyl and titanium nitride from amino complexes of titanium (9, 10).

## 3. CVD EQUIPMENT

A simple CVD unit is shown in Fig. 3. A carrier gas is passed over the volatile source, which is held at a specified temperature defined by its vapour pressure, then mixed with the reducer gas before passing over the hot substrate. The temperature of the transport tube between evaporator and reactor should not fall below the evaporation

temperature so as to avoid condensation and care needs to be taken to avoid the reaction occurring homogenously in the gas stream. The distance between evaporation and reactor should be as long as necessary to ensure complete mixing of the reactants which occurs more rapidly at high temperatures.

Much laboratory equipment is built out of glass because of its convenience and corrosion resistance. In general only one or two samples are coated at the time. In a preliminary development stage towards industrial use, possibly up to e.g. 100 samples would be coated depending on their size in order to test out the reproducibility and uniformity of the coating and its properties. The step to an actual industrial reactor of the type shown in Fig. 4a, is quite large: 4,000 - 25,000 cutting tool tips can be coated according to reactor size. Such industrial installations are generally of metallic construction and great care needs to be exercised in the choice of materials because of corrosiveness of reactants and side-products (HCl, HF etc.) and the industrial requirement of a long lifetime for the installation. Two standard CVD problems become considerably enhanced in such industrial reactors; both are concerned with gas flow. The first is that the gas flows become diluted due to depletion of the reactant gases on the one hand and to the concomitant generation of side-products such as HCl on the other. The second is that the gas flow should be maintained in a semi-turbulent condition during its passage through the reactor to ensure that the substrate can be reached by the reacting gases to give a completely uniform coating overall. A gas flow schematic is given in Fig. 4b where the extensive ancilliary equipment for gas purification (to better than 1 vol. ppm in oxygen and water vapour) and accurate metering is apparent. In this case a neutralizing fluid ring pump is used to deal with the HCl side-product of the CVD reaction.

A high temperature CVD reactor is illustrated in Figure 5. This type of equipment has been used for the formation of pyrolytic graphite and pyrolytic boron nitride as free standing bodies. The operating temperature is between 1500°C and 2500°C.

The reaction chamber components are graphite and are heated inductively by a water-cooled coil. It is supported on a graphite and nickel column which also acts as the reactant gas inlet to the chamber. The spent gases escape from the top of the reaction chamber into the outer steel chamber from which they are removed by continuous pumping. The temperature of the reaction chamber is measured optically along the gas inlet tube and also by means of thermocouples embedded in the outer susceptor.

With pyrolytic boron nitride, crucible-shaped graphite moulds are placed in the chamber so that crucibles can be grown on the exterior surfaces of the moulds. This is successful because the thermal coefficient of expansion of most graphites is greater than that of PBN. The PBN fits the graphite mould exactly at the deposition temperature, but on cooling the graphite shrinks away from the PBN so that the crucible becomes detached. Providing that the surface of the graphite mould is polished before deposition and there is a slight angle (1-2°) of taper on the mould, the release of the PBN crucible presents no problem.

Small tubes (up to 25mm) are readily made externally in the same way as crucibles. However, large tubes present a more difficult problem. When their diameter approaches that of the deposition chamber they must be made internally on a large graphite sleeve. The thermal mis-match between the PBN and graphite on cooling is overcome by scoring the graphite sleeve so that it is the weaker component. On cooling, the boron nitride should rupture the graphite sleeve without suffering damage, but this is not always successful.

The most convenient reactants are in gaseous form such as $BCl_3$, $CO_2$ or $H_2$ (and argon as carrier) as these are easily metered provided that any potential corrosiveness is borne in mind when designing an installation. This is one reason, for example, for the use of $WF_6$ in the deposition of tungsten. Tungsten hexafluoride boils at 19°C and can therefore be handled as a gas at normal room temperatures.

It is also convenient to use a liquid source for the chloride vapour if it is available. A standard example is $TiCl_4$ which has a high vapour pressure in the range 80-100°C as shown in Fig. 6. A carrier gas is then passed through the liquid held at the appropriate temperature (as indicated schematically in Fig. 4b).

Solid vapour sources in fine or coarse powder form can be used in the case of $TaCl_5$ (Fig. 6) but care needs to be taken to ensure both that the carrier gas is fully saturated and that no powder is carried away in the gas stream. It is sometimes convenient to use the CVD reaction in reverse to obtain a chloride source. This is often done with tantalum by passing chlorine or HCl over chips of the metal (Fig. 1). A further example is found in

$$VCl_2 + H_2 \overset{K}{\rightleftharpoons} V + 2\ HCl \qquad - 14$$

As shown in Fig. 6, $VCl_2$ has an appreciable vapour pressure only in the region of 1,000°C. As an alternative to using solid $VCl_2$ as a source, the metal can be chlorinated to produce a $VCl_2$ solid intermediate product.[2] Following the type of approach discussed above, under a mixture of $H_2$ and HCl the partial pressure of $VCl_2$ over metallic vanadium varies with the square root of the reaction constant as shown in Fig. 7

$$K = \frac{P^2_{HCl}}{P_{H_2}}$$

for a temperature of about 1,000°C. Under the conditions on the left of the diagram, gaseous $VCl_2$ is produced directly. Under the conditions at the right, solid $VCl_2$ is formed first as a coating on the source metal over a wide range of K values with the vapour pressure given by the curve in Fig. 7.

## 4. RANGE OF MATERIALS PRODUCED BY CVD

Tables 1 and 2 give some indication of the range of elements and compounds which have been formed by CVD. Although there are very few metallic elements which cannot be obtained by CVD, the method is of much greater practical significance for those elements which cannot be readily deposited by other methods. This applies particularly to the refractory metals, which for reasons of either chemistry, brittleness or high melting point cannot be electroplated, mechanically worked, thermally sprayed, or vacuum evaporated. These materials can be deposited by CVD in layers up to several millimetres thick using temperatures which, in comparison with their melting points, are extremely modest. Temperatures in the range 300-1500°C have been used for depositing W and Re, both of which have melting points in excess of 3000°C.

Although the temperatures employed in CVD may be low by the standards of the refractory metals, it must be admitted that the temperatures used are rather high compared with most other coating processes. An examination of Table 1 shows that there is no process which operates at less than 200°C and a more typical process temperature is in the range of 700-1100°C. This is a major limitation of the CVD process. Many substrates such as plastics, die casting alloys and brasses cannot be coated by CVD for this reason; often substrates such as steels cannot be coated without careful regard of their metallurgical properties. Frequently a recovery heat-treatment is necessary to restore the substrate properties.

The high temperatures involved in CVD are not always disadvantageous because there are some materials which develop important properties when formed by a very high temperature. An excellent example is pyrolytic graphite, formed by the thermal decomposition of hydrocarbons at temperatures around 2000°C. It has properties which are quite different from conventional graphite. Pyrolytic graphite has a higher density, lower porosity, greater strength and higher thermal conductivity.

CVD is not restricted to pure elements. It finds some of its more important applications in the deposition of compounds (see Table 2). Boron nitride, silicon nitride and boron carbide are all produced by CVD in forms, which, like pyrolytic graphite, have properties not found when the materials are made by other methods. A number of very important carbides are produced by CVD, and these are generally used as wear-resistant coatings on cutting tools and in sliding wear situations. Titanium carbide and chromium carbide are the most widely used hard coatings. These layers are extremely brittle and can only be deposited as very thin coatings.

It would be very desirable to incorporate into these deposits another material which would improve the toughness of these layers without a great loss in their hardness. For example, the introduction of cobalt would be expected to improve the toughness of these layers by anology with the composites of WC/TiC with Co which are made by power metallurgy. However, this illustrates a limitation of CVD because the co-deposition of dissimilar materials is very difficult to achieve by CVD. The reasons for this are that the conditions required for each CVD reaction are very specific and the reagents tend to interact with each other. For example, if cobalt acetylacetonate is introduced into a gas stream containing tungsten hexafluoride with the aim of co-depositing tungsten carbide with cobalt, cobalt fluoride is readily formed which condenses out without being reduced to cobalt metal. In contrast tungsten/rhenium mixtures have been successfully produced when both metals were transported as fluorides, but, in general, mixtures cannot be produced[11].

## 5. CVD PROCESSES

Amongst the pure metals which may be deposited by CVD, it is probable that tantalum and tungsten are of the greatest practical importance. Tantalum is transported as the chloride and may be deposited on steel to form an extremely impervious layer which has excellent corrosion resistance. Figure 8 shows a small steel probe coated in tantalum, but industrial use is now concentrating on the coating of the internal bores of tubing. This is an application for which CVD is particularly suitable because it is possible to use the tube itself to contain the reactant gas flow. This minimises the redundant plating and also makes possible the coating of surfaces which would be very difficult to reach with any other technique.

Tungsten and, to some extent, rhenium deposits are interesting because they are produced with an adequate thickness to be self-supporting. Figure 9 shows some free-standing tungsten tubes which have been separated from the original substrate. The deposition of tungsten has been studied chiefly for its use in rocket motor nozzles. These nozzles are subject to very high temperature erosion for short periods, and in a reducing rocket flame CVD tungsten performs very well. It is generally deposited on graphite.

Vanadium and chromium deposited on to steel at about 1000°C react with carbon drawn from the substrate to form hard wear resistant VC or $Cr_7C_3$ coatings. The carbon loss is compensated by diffusion from deeper lying material in the substrate so that the steel surface regions are not softened (except in very thin steel parts). As the

stoichiometry range of both carbides in equilibrium with steels, at such temperatures, is extremely narrow, coatings of reproducible composition and quality are readily made.

A major industrial application of CVD is to produce a TiC hard coating for sintered carbide WC-Co cutting tools. The process can also be used to coat steels but this has a problem for high precision components because of the high deposition temperature of about 900°C. Steel substrates become softened during deposition and must then be re-hardened unless they are air hardening and can then be quenched in the reactor on cooling. During the hardening and tempering process it is normal that some small amount of distortion will occur but which cannot be corrected by grinding or lapping because of the coating. A number of attempts have been made to deposit hard layers at temperatures sufficiently low to avoid degrading steel substrates. Titanium carbonitride has been deposited from $TiCl_4$ and $NMe_3$ at temperatures around 700°C, but this does not appear to have been exploited because the process temperature is still rather too higher (10).

A more suitable wear-resistant coating for normal steels, copper, and copper alloys is tungsten carbide. Coatings of $W_2C$ on steels have been deposited from the chemical mixture following reaction 3 in the temperature range 400°-700°C. Recently, the deposition temperature has been reduced to about 300°C, and coatings consisting of $W_2C$ and a new form of tungsten carbide, $W_3C$, have been obtained. The microhardness of the tungsten carbide coatings produced in this temperature range is 1800-2700 kg/mm$^2$. It has been shown that the formation of $W_3C$ is more favourable at the lower temperatures. The hardness of $W_3C$, however, is about the same as that of $W_2C$ (12).

It is not widely recognised that the pack metallising processes of aluminising and chromising are examples of chemical vapour deposition. However, recent experiments in which the substrate and the pack have been separated completely have demonstrated that vapour transport is a major mechanism in the metallising process. Aluminising via the pack cementation method requires the specimens to be buried in a powder pack consisting of aluminium source material, halide activator and inert diluent (13). A typical pack might contain 15 wt% aluminium powder.

The aluminising system is heated in an inert atmosphere to a temperature in the range 750-1050°C. In the heated system aluminium enters the gaseous phase as a monohalide vapour. This vapour reacts with the substrate, usually nickel or steel, to produce aluminide surfaces. The deposited aluminium diffuses into the substrate alloy, and so permits the continued deposition of aluminium as the system seeks to equalize the aluminium activities associated with the source material and the surface aluminide. With a nickel substrate the basic reaction sequence (Fig. 10) can be written as:

$$NH_4X \rightarrow NH_3 + HX \qquad - 15$$

$$2Al + 6HX \rightarrow 2AlX_3 + 3H_2 \qquad - 16$$

$$AlX_3 + 2Al \rightarrow 3AlX \qquad - 17$$

$$3AlX + 2Ni \rightarrow 2NiAl + AlX_3 \text{ (or other stoichiometry of } Ni_xAl_y\text{)}. \qquad - 18$$

The process is normally performed at atmospheric pressure. In practise an aluminide coating may consist of various phases (e.g. $Al_3Ni$, $Al_3Ni_2$, NiAl and $Ni_3Al$), each having its own composition range. The outer coating is normally more aluminium rich than the coating near the substrate. The most effective phase for oxidation resistance is the NiAl phase.

This process is widely used on gas turbine blades because it gives good high temperature oxidation resistance. In terms of the numbers of components metallised in this way, aluminising is probably the second largest volume use of CVD after titanium carbide.

CVD is becoming more widely used as a method for producing materials with special properties. For example, the Rathyeon Corporation is now producing slabs of zinc sulphide and selenide up to 25mm thick which have extremely good infra-red transmittance. These are produced by CVD presumably by the reaction between zinc vapour and a sulphide, probably $H_2S$. Pyrolytic boron nitride is another example of a material which can be formed by CVD with special properties (14). Hexagonal boron nitride is a very stable and involatile compound and therefore almost any high-temperature reaction between compounds of boron and nitrogen tends to yield boron nitride. The compounds most usually employed as a source of boron are diborane, $B_2H_6$, the boron halides, $BX_3$, borazole, $B_3N_3H_6$, and B-trichloroborazole, $B_3N_3H_3Cl_3$. Ammonia is the most usual source of nitrogen. Nitrogen itself has been used but it reacts very much more slowly than ammonia. At temperatures greater than those indicated in reactions 19-21 the

$$B_2H_6 + 2NH_3 \xrightarrow{>500^\circ C} 2BN + 6H_2 \qquad - 19$$

$$BCl_3 + NH_3 \xrightarrow{>1000^\circ C} BN + 3HCl \qquad - 20$$

$$B_3N_3H_3Cl_3 \xrightarrow{>1300^\circ C} 3BN + 3HCl \qquad - 21$$

only product is boron nitride, but at lower temperatures various side-reactions occur, leading to products which still contain some hydrogen. Borazole gives a polymeric $(BNH)_x$ compound at 500°C which is only converted into BN above 800°C. Similarly B-trichloroborazole gives an unsatisfactory product at temperatures below 1300°C. The reaction

between boron halides and ammonia is complicated at temperatures below 1000°C by an addition product. The reaction between diborane and ammonia is most suitable for producing BN at temperatures in the range 700-1250°C. Below 1000°C it appears to yield amorphous BN, which is not very stable and which decomposes if subsequently heated above 1000°C. However, diborane and ammonia above 1000°C yield polycrystalline BN, which is much more stable.

The structure of PBN is very much related to the temperature at which it is formed. At temperatures below 1000°C the product is amorphous, while at temperatures in the range 1000-1200°C a polycrystalline structure starts to develop which is believed to be turbostratic. The $B_3N_3$ hexagons are packed in layers parallel to the substrate but otherwise their orientation is random. Above 1300°C the hexagonal structure begins to develop an increasing degree of order, and highly ordered material with densities approaching the theoretical X-ray value of 2.270g $cm^{-3}$ are obtained at 1700-2100°C. It is not practical to prepare BN at temperatures much in excess of 2100°C because its dissociation pressure becomes significant. Boron nitride grown at temperatures above 1800°C has very pronounced anisotropic properties, but material grown in the temperature range 1300-1700°C has been reported to have an isotropic structure.

The deposition pressure and the reactant flow rates also have an important influence on the properties of vapour-deposited boron nitride. Low pressures have been found to be important in avoiding the formation of powdery deposits. Pressures as low as 0.5 Torr have been used, although pressures in the range 5-50 Torr are more common. It is also important to control the rate of deposition to achieve a high-density product. Control of deposition rate has been obtained both by restricting the flow of one reagent and by dilution with an inert carrier gas.

PBN is best formed by the reaction between a boron halide and ammonia in the temperature range 1800-2000°C. This is not the only temperature range in which PBN is formed, but over this range material of high density, good orientation and low contamination is produced. PBN can be deposited on graphite moulds in layers up to 2mm thick so that when the coating is released, a free-standing piece of PBN is obtained as discussed above. By this method plates, crucibles, tubes and boats can be made as shown in Fig 10. The metallic impurity level in these deposits is usually not more than 30 p.p.m. This is partially because high purity reagents and graphite substrates are used and partially because most other materials are transported away from the hot zone under the conditions which form PBN.

PBN is an extremely suitable material for use in microwave travelling wave tubes The essential part of the travelling wave tube is a carefully spaced coil which is often made from molybdenum because of the high temperature at which it operates. Accurately machined PBN rods are used to support the coil, in order to insulate it from the vacuum envelope, and conduct heat away rapidly. The rods are cut from plates of PBN so that the thermal conductivity is good in the radial direction and also along the length of the rod.

## 6. SUMMARY

CVD has most to offer under the following circumstances:-

1) When the material to be deposited is refractory in nature (e.g. high melting point carbide or nitride).
2) When the surface to be coated is geometrically complex ( e.g. inside of a control valve).
3) When the nature of the substrate imposes no limitation on the process temperature.
4) When a particular structure is required in the deposit (e.g. pyrolytic graphite).
5) When large numbers of small components are to be coated.

## REFERENCES


1. U.S. Patent 455 230 (1891) to L. Mond.

2. A.E. van Arkel and J.H. de Boer, Z. anorg. allg. Chem., 1925 145 345.

3. F.A. Glaski, Proc. 4th Int. Conf. on Chemical Vapour Deposition, The Electrochemical Society, 1973, 521.

4. N.J. Archer, Proc. 5th Int. Conf. on Chemical Vapour Deposition, The Electrochemical Society, 1975, 556.

5. J. Chin, P.K. Gantzel and R.G. Hudson, Thin Solid Films, 1977, 40, 57.

6. H.H. Kellogg, Trans AIME, 1950 188 862.

7. E. Steinmetz and H. Roth, J. Less Common Metals 1968 16 295.

8. H. Gass and H.E. Hintermann, Thin Solid Films, 1977, 40, 81.

9. R. Breining, W.M. Bolton and F.O. Deutscher, Ger. 1,235,106, Feb. 23, 1967.

10. J.A. Bloom, G.F. Wakefield and C.L. Yaws, Proc. 4th Int. Conf on Chemical Vapour Deposition, The Electrochemical Society, 1973.

11. W.R. Holman and F.J. Huegel, Proc. 2nd Int. Conf. on Chemical Vapour Deposition, The Electrochemical Society, 1970, 171, 1974.

12. N.J. Archer and K. Yee, Wear, 1978, 48, 237.

13. S.R. Levine and R.M. Caves, J. Electrochem. Soc., 1974, 121, 1051.

14. N.J. Archer, "High Temperature Chemistry of Inorganic and Ceramic Materials", ed. F.P. Glasser and P.E. Potter, The Chemical Society 1977, 167.

TABLE 1.

Metals formed by CVD

| Material | CVD Method | Temp. (°C) |
|---|---|---|
| Aluminium | As metal. Thermal decomp. $AlR_3$, $AlHR_2$ (R=alkyl) | 200-250 |
| | As aluminide Al + $AlX_3$ (X-halide) in $Al_2O_3$ bed | 700-1000 |
| | $AlCl_3+H_2$ | 900-1000 |
| Antimony | Thermal decomp. $SbCl_3$ | 500-600 |
| | Thermal decomp. $SbH_3$ | ~150 |
| Arsenic | Thermal decomp. $AsCl_3$ | 300-500 |
| | Thermal decomp. $AsH_3$ | 230-300 |
| Boron | Thermal decomp. $H_2H_6$ | 400-500 |
| | Thermal decomp. $B\ Br_3$ | 1000-1300 |
| | $BCl_3+H_2$ | ~1500 |
| Bismuth | Thermal decomp. $BiCl_3$ | ~250 |
| | Thermal decomp. $BiH_3$ | 230-300 |
| Carbon | Thermal decomp. of hydrocarbons e.g $CH_4$ as carbon | 1000-1500 |
| | $C_2H_6$, $C_2H_4$, $C_2H_2$ as graphite | 1500-2500 |
| Chromium | As metal. Thermal decomp of $CrI_2$ | 900-1000 |
| | Thermal decomp. of $Cr(CO)_3$ and dicamene chromium | |
| | As chromium diffusion layer Cr + Halide Activated e.g. $NH_4Cl$ in $Cr_2O_3$ bed | 400-1200 |
| Cobalt | Thermal decomp. $Co(acac)_{2\ or\ 3}$ | 300-500 |
| Copper | As metal. Thermal decomp. Cu $(acac)_2$ | 260-450 |
| | As copper layer on steel $Cu_3Cl_3+Fe \rightarrow Cu+FeCl_3$ | 500-1000 |
| Germanium | Disproportion $GeI_2 \rightarrow Ge+GeI_4$ | ~450 |
| | Thermal decomp. $GeH_4$ | 400-1100 |
| Gold | Thermal decomp. $AuCl.PPh_3$ | |
| | Disproportion $AuCl_2 \rightarrow Au+Au_2Cl_6$ | |
| Hafnium | Thermal decomp. $HfX_4$ (X=I), Br) | 1100-1450 |
| Lead | As powder from thermal decomp. of $PbEt_4$ | 300-500 |
| Molybdenum | $MoX_5$ or $MoF_6$ + $H_2$ | ~650 |
| | $Mo(CO)_5$ + $H_2$ | 300-600 |
| Nickel | Thermal decomp. $Ni(CO)_4$ | 180-200 |
| | Thermal decomp. $Ni(acac)_2$ | 350-450 |
| Niobium | $NbCl_5$ + $H_2$ | 1000-1400 |
| Osmium | $Os_3Cl_4$ + $H_2$ | |
| | Thermal decomp. $Os_5(CO)_3Cl_2$ | 325-340 |
| Palladium | Thermal decomp. $Pd(acac)_2$ | 350-450 |
| Platinum | Thermal decomp. $Pt(CO)_2Cl_2$ | ~600 |
| | Thermal decomp. $Pt(acac)_2$ | 350-450 |
| | $ReF_5$ + $H_2$ | 250-1100 |
| Rhenium | $ReCl_5+H_2$ | 600-1200 |
| | Thermal decomp. $ReOCl_4/ReCl_5$ | 1250-1500 |
| Rhodium | Thermal decomp. $Rh(CO)_2Cl_2$ | |
| Ruthenium | Thermal decomp. $Ru(CO)_5$ | 200 |
| | Thermal decomp. $Ru(CO)_2Cl_2$ | |
| Silicon | $SiCl_4+H_2$ | 900-1800 |

TABLE 1. (Continued)

| Material | CVD Method | Temp. (°C) |
|---|---|---|
| Silicon | $SiHCl_3+H_2$ | 900-1800 |
| | $SiHCl_3+H_2$ | 950-1250 |
| Tantalum | $TaCl_5+H_2$ | ~1000 |
| Tin | $SnCl_2+H_2$ | 400-600 |
| Titanium | $TiCl_4+H_2$ | 1100-1400 |
| | Thermal decomp. $TiI_4$ | 1200-1500 |
| Tungsten | $WF_6+H_2$ | 400-700 |
| | $WCl_6+H_2$ | 600-700 |
| | $W(CO)_6$ | 350-600 |
| Tungsten/ Rhenium | W+Re fluoride + $H_2$ | 400-1000 |
| Uranium | Thermal decomp. $UI_6$ | 1500 |
| Vanadium | $VCl_2+H_2$ | 800-1000 |

TABLE 2

Compounds formed by CVD

| Materials | | CVD Method | Temp. (°C) |
|---|---|---|---|
| Nitrides | BN | $BCl_3+NH_3$ | 1000-2000 |
| | | Thermal decomp. $B_3N_3H_3Cl_3$ | 1000-2000 |
| | HfN | $HfCl_x + N_2 + H_2$ | 950-1300 |
| | $Si_3N_4$ | $SiH_4+NH_3$ | 950-1050 |
| | | $SiCl_4+NH_3$ | 1000-1500 |
| | TaN | $TaCl_5+N_2+H_2$ | 2100-2300 |
| | TiN | $TiCl_4+N_2+H_2$ | 650-1700 |
| | VN | $VCl_2+N_2+H_2$ | 1100-1300 |
| | ZrN | $ZrCl_4+N_2+H_2$ | 2000-2500 |
| Oxides | $Al_2O_3$ | $AlCl_3+CO_2+H_2$ | 800-1300 |
| | $SiO_2$ | $SiH_4+O_2$ | 300-450 |
| | | Thermal decomp. $Si(OEt)_4$ | 800-1000 |
| Silicon oxynitride | | $SiH_4+H_2+CO_2+NH_3$ | 900-1000 |
| | $SnO_2$ | $SnCl_4+H_2O$ | |
| | $TiO_2$ | $TiCl_4+O_2$+ Hydrocarbon (flame) | |
| Silicides | $V_3Si$ | $SiCl_4+VCl_4+H_2$ | |
| | MoSi | Mo (substrate) + $SiCl_2$ | 800-1100 |
| Borides | $AlB_2$ | $AlCl_3+BCl_3$ | ~1000 |
| | $HfB_x$ | $HfCl_4+BX_3$ (X=Br,Cl) | 1900-2700 |
| | $SiB_x$ | $SiCl_4+BCl_3$ | 1000-1300 |
| | $TiB_2$ | $TiCl_4+BX_3$ (X=Br,Cl) | 1000-1300 |
| | $VB_2$ | $VCl_4+BX_3$ (X=Br,Cl) | 1900-2300 |
| | $ZrB_2$ | $ZrCl_4+B\ Br_3$ | 1700-2500 |
| Carbides | $B_4C$ | $BCl_3+CO+H_2$ | 1200-1800 |
| | | $B_2H_6+CH_4$ | |
| | | Thermal decomp of $Me_3B$ | ~550 |
| | $Cr_7C_3$ | $CrCl_2 + H_2$ | 1000 |
| | $Cr_3C_2$ | $Cr(CO)_5+H_2$ | 300-650 |
| | HfC | $HfCl_4+H_2+C_7H_8$ | 2100-2500 |
| | | $HfCl_4+H_2+CH_4$ | 1000-1300 |

TABLE 2. (Continued)

| Materials | | CVD Method | Temp. (°C) |
|---|---|---|---|
| $Mo_2C$ | $Mo(CO)_6$ | | 350-475 |
| | $Mo+C_3H_{12}$ | | 1200-1800 |
| SiC | $SiCl_4+C_6H_5CH_3$ | | 1500-1800 |
| | $MeSiCl_3+H_2$ | | ~1000 |
| TiC | $TiC_4+H_2+CH_4$ | | 980-1400 |
| $W_2C$ | Thermal decomp. $W(CO)_6$ | | 300-500 |
| | $WF_6+C_6H_6+H_2$ | | 400-900 |
| VC | $VCl_2+H_2$ | | 1000 |

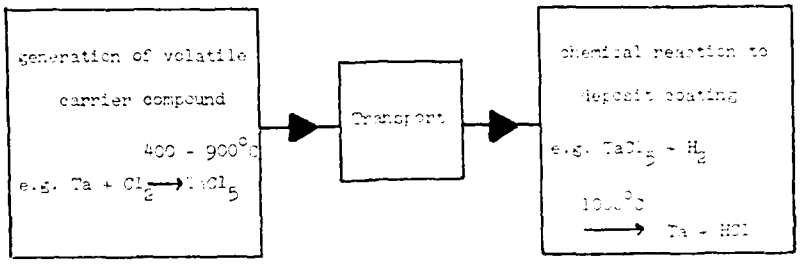


Fig. 1. Basic Steps in a CVD process (Showing CVD of tantalum as an example).

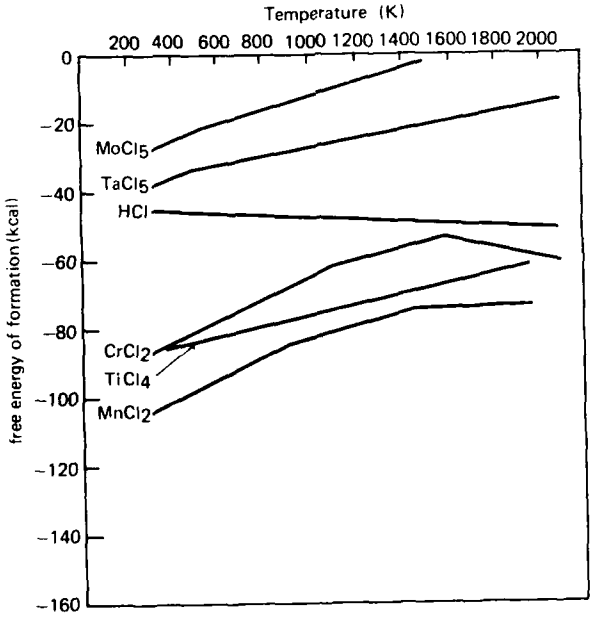


Fig. 2. Ellingham diagrams showing the free energy of formation per mole of various chlorides as a function of temperature.

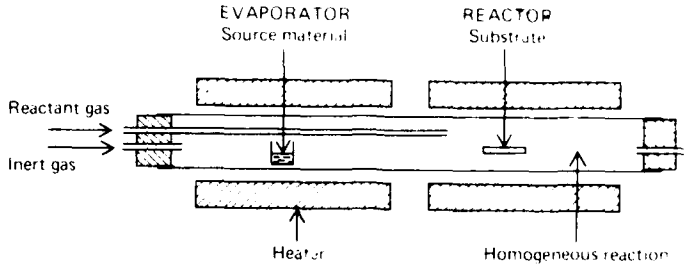


Fig. 3. Schematic representation of CVD reactor.

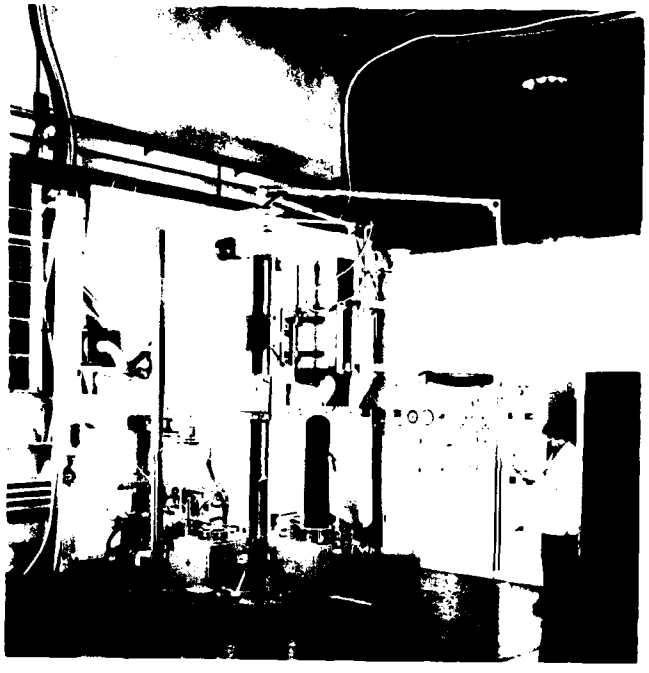

Fig. 4a. Industrial CVD Installation (courtesy Berna-Bernex AG).

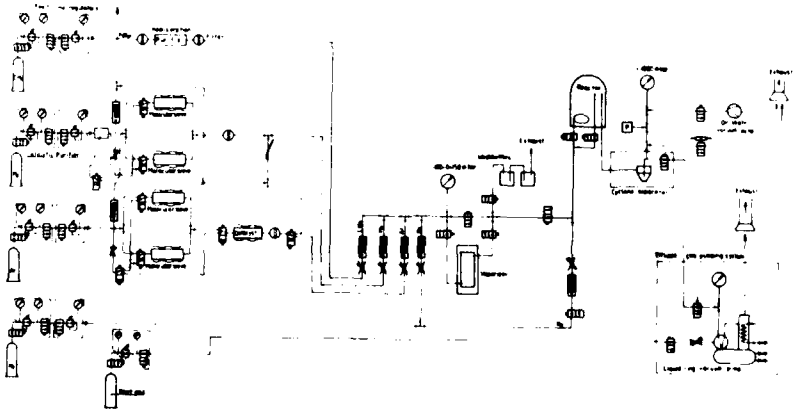

Fig. 4b. Gas flow diagram for TiC and TiN coatings.

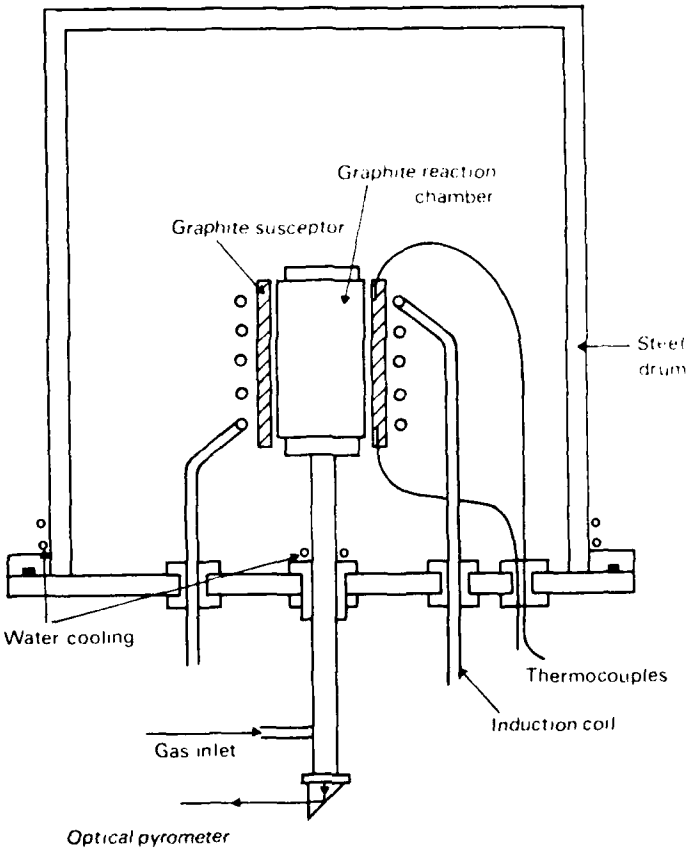


Fig. 5. High temperature CVD reactor (for CVD of pyrolytic boron nitride).

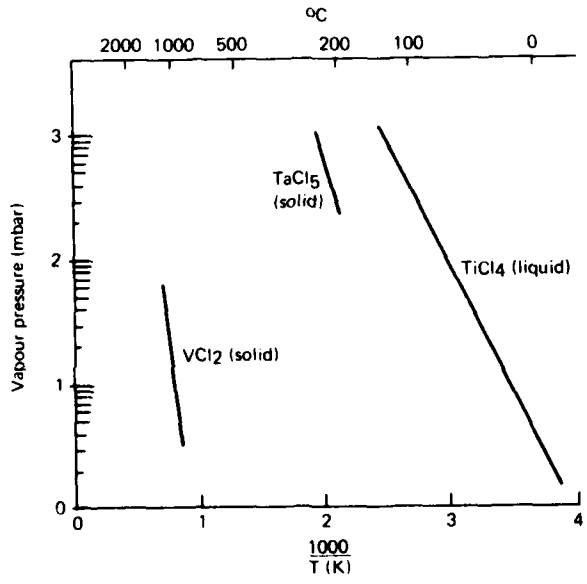


Fig. 6. Vapour Pressure of selected chlorides as a function of reciprocal absolute temperature.

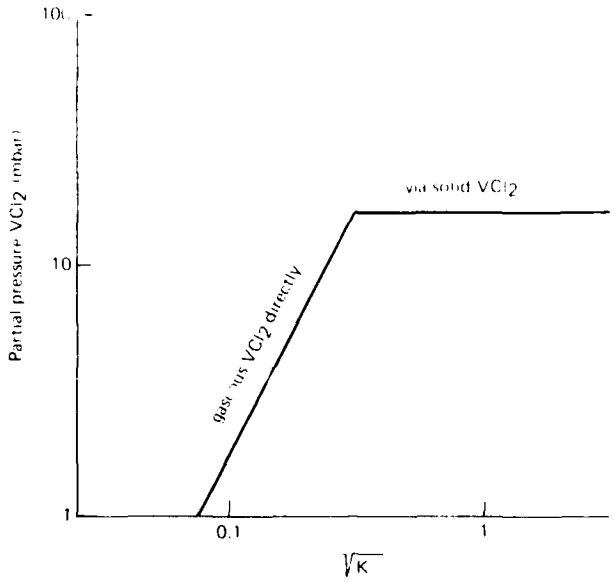


Fig. 7. Partial pressure of $VCl_2$ formed by chlorinating vanadium at 1000°C, either directly as a chloride gas or via an intermediate solid phase.

Fig. 8. Steel probe coated with CVD tantalum.

Fig. 9. Tungsten tubes formed by CVD.

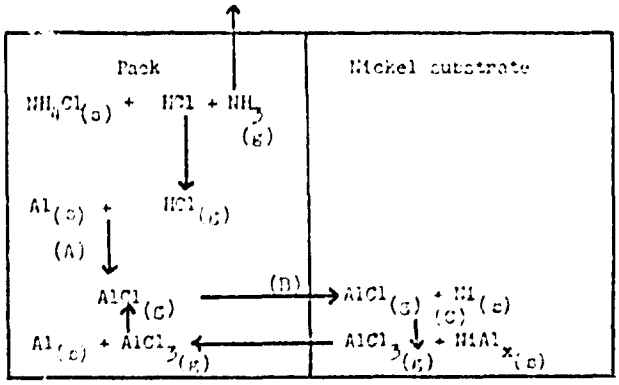


Figure 10. CVD reaction scheme for the aluminising of nickel.

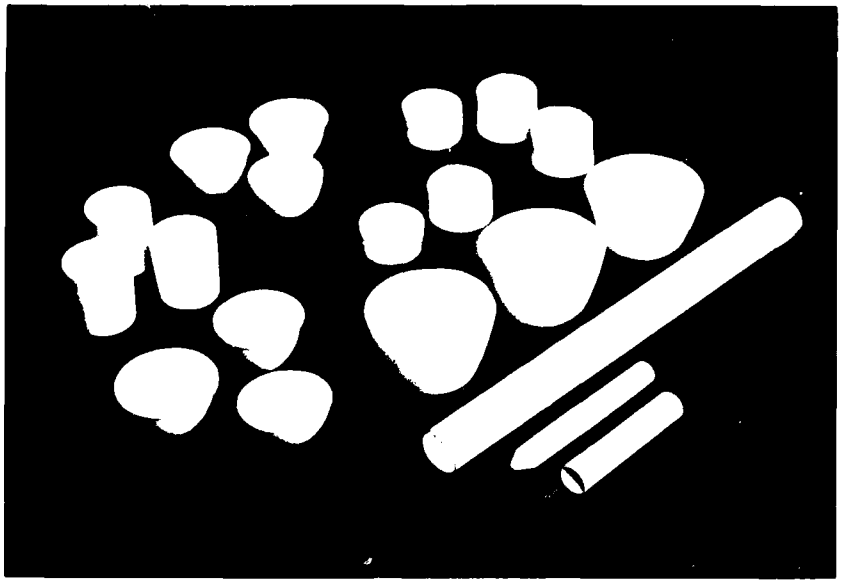

Fig. 11. Pyrolytic boron nitride components formed by CVD.

# Sprayed Coatings

by

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SUMMARY

Thermal spraying has turned out to be an efficient means for the protection of surface areas against elevated temperature, wear, corrosion, hot gas corrosion and erosion in structural aircraft components. Particularly in jet engines numerous parts are coated by flame, detonation or plasma spraying technique. Development of new technologies and materials give rise to assume that thermal spraying techniques will gain more and more significance in aircraft and aerospace industries, as they provide excellent results, especially against wear and hot gas corrosion.

In the paper, the applied methods of flame, detonation and plasma spraying will be explained. Electric arc spraying is applied too, but much less as compared to other processes.

Possibilities to spray coatings which meet aircraft service requirements will be discussed, as well as methods for quality control, expecially non-destructive test methods. In particular, coating characteristics and properties obtained by different spray methods will be described, and special attention is paid to low pressure plasma spraying (LPPS).

## 1. INTRODUCTION

Thermal spraying has now reached a stage in its development, at which it is used even for coating highly-stressed or key structural components. In jet engines, numerous parts are sprayed by flame, detonation or plasma process. One of the recent developments in plasma spraying provides working under controlled atmosphere at low pressure and permits to produce sophisticated coating systems. Under service conditions, they are able to meet the requirements for highly loaded engine components, such as turbine rotor blades, by protective hot gas corrosion coatings of the MCrAlY-type.

The significance of thermal spray processes may be proved by the fact that a single engine may employ as many as 600 coated parts. It must be admitted that spray deposits have sometimes fallen into disrepute as a result of incorrect applications. Therefore, the very efficient spray techniques should be applied only if they offer advantages, and never if other techniques are more useful.

E. g. by the use of thermally sprayed coatings the life of aircraft jet engines has successfully been extended. Thus one of the major problems facing the airline industry has partially been solved, namely the wear of non-lubricated mating parts of mechanical components resulting from vibration, fretting, impact and hammer wear during engine operation. In other areas of a jet engine, ceramic/metallic thermal barrier coatings are used in order to reduce metal operating temperatures and the effects of thermal transients on combustion chambers. In other cases, sprayed coatings have to serve as a means for corrosion protection or wear resistance such as heat or air barriers and for repairing components.

As to the various spray processes, thermal spraying generally is based on methods by which a metallic or non-metallic wire or powder is melted. The fused particles are projected onto a prepared surface so as to build up an adherent coating.

The thermal energy necessary to melt the spraying material can be produced in different ways. Flame and plasma spraying as well as detonation plating are at present the mostly applied thermal spray procedures in aerospace industries. Particularly plasma spray deposition has been developed as a practicable processing technique for the last ten years. Electric arc spraying is applied too, but much less as compared to the other processes mentioned above.

## 2. SURFACE PREPARATION

The conventional thermal spraying procedures require a very conscientious surface preparation, which takes usually one of the following forms [1]:

1. Mechanical preparation by lathe turning. This may be either
   - "rough turning", producing a plain diameter with speeds and feeds such as to produce a relatively coarse surface or
   - a rough turned 60 °V thread, with normally one thread per millimeter, followed by application of a special rotary shaft preparing tool, which is used to break up the sharp peaks of the thread. This method is normally for heavy coatings built up on large components [1]. Rough lathe turning methods can generally not be recommended in aircraft components as dynamical properties may considerably deteriorate.

2. Grit blasting. Grit blasting is often carried out utilizing either pressure or suction blast equipment.

By pressure blasting, the blasting grit is introduced into a stream of compressed air and fed via a hose to the workpiece, where the grit emerges from the nozzle in the air stream, and impinges upon the workpiece. Selection of a suitable grit is dependent both upon the substrate material and the coating to be deposited. In suction blasting, a compressed air stream siphons the blasting media to the exit nozzle, as opposed to gravity introduction used in the pressure blasting method.

Angular steel grit is normally selected for relatively soft substrate materials, and where a relatively coarse grit blast surface is called for. With this type of grit, dulling of the edges takes place with use, which results in progressively poorer preparation. Aluminium oxide grit is normally chosen for harder substrate materials, or in instance where a fine grit blasted surface preparation is required. Aluminium oxide grit is used in various grades, the finer ones producing a smoother surface. Fine blasted surfaces are normally used in combination with plasma deposition of those powders bound for a fine as-sprayed surface finish. Typically, such coatings would go into service in either the as-sprayed condition, or with the very minimum of finishing such as an abrasive brushing technique.

Aluminium oxide particles break down in use, thereby exposing new sharp edges. However, it should be noted that this breakdown results in the grit becoming progressively finer, thereby producing finer blasted surfaces. It is apparent, therefore, that the choice of grit blast media is important in defining a coating system. It is also important that the grit condition is continually observed, and that the grit should be clean and free of grease or other contamination. This requirement dictates that the air supply should also be free of contaminants [1].

## 3. SPRAYING METHODS AND COATING PROPERTIES

### 3.1 FLAME SPRAYING

#### 3.1.1 PRINCIPLE OF THE FLAME SPRAYING PROCESS

In flame-spraying, the consumable wire or powder is fused by a oxy-fuel gas flame (Fig. 1). Wire is fed at a controlled rate into the flame, which melts the wire tip. Compressed air is fed through an annulus around the outside of the nozzle, which accelerates the molten or semi-molten particles on the substrate. Fuel gases commonly used are acetylene and propane. Air and gas flows and pressures, together with wire diameter and wire feed rate, influence the coating properties. In modern equipment, all these parameters are accurately controlled, and defined by the requests of the particular coating in question. Wire is fed into the spray head by means of drive rollers, which may be powered by an air turbine or variable speed electric motor, suitably geared down. In comparison to the powder flame spray process, flame spraying utilizing wire is economical, and with its long history is used extensively in a wide variety of industries. It should be noted, however, that the process is limited to materials which can be produced in a suitable wire form, and is also limited to materials which can be melted in a combustion flame [1].

Powder flame spraying process extends the choice of materials to those which can be produced in powder form. This leads to the use of various carbides, oxide ceramics, cermets, etc. Figure 1 b indicates a schematic layout of a combustion powder spraying gun, illustrating the oxy-fuel gas flame into which powder is introduced suspended in a carrier gas. The powder may be introduced either by gravity, or by a more sophisticated pressurised supply.

In this process, the fuel gases commonly used are acetylene or hydrogen. The carrier gas the powder is suspended into, may be oxygen, fuel gas, or air, or some other usually inert gas. The combustion flame may be shrouded with a stream of compressed air or inert gas, which may be convergent, divergent, or parallel in flow. Again, the spray parameters, for a particular material, will define the choice of gases, the geometry of the spray head, gas and powder flows, etc.

### 3.1.2 COATING PROPERTIES

Flame sprayed coatings are normally used in thicknesses ranging from about 50 microns to as high as some millimeters. The required coating thickness will often play a major part in selection of a suitable coating. Although flame spraying can be used for corrosion prevention at ambient and elevated temperatures and for salvage of worn or mismachined parts, the most prevalent use of the process is in providing resistance to wear, abrasion or erosion. Thermal barrier coatings sprayed by the oxy-acetylene process have gained special importance. Such ceramic/metallic coatings are widely used in gas turbine engines to reduce metal operating temperatures and the effects of thermal transients on combustion chambers, transition ducts and after burner liners [2].

In general, the desired properties of a practical thermal barrier coating are [2]:

- low thermal conductivity
- a close match of the thermal expansion characteristics of the ceramic and metallic components of the coating and the substrate alloy
- resistance to concentrated mechanical stresses which result in cracking and promote loss of coating
- adequate stabilization of the thermal crystal structure
- high reflectivity
- maximum oxidation/hot corrosion resistance of the metallic constituent of the coating
- reparability during manufacturing and at overhaul after field service operation.

Several flame sprayed ceramic/metallic thermal barrier coating systems based on magnesia stabilized zirconium oxide have been successfully applied over the past fifteen years. In the present, increased demands for higher gas turbine performance necessitate the development of improved thermal barrier coatings. The two- or three-layer flame sprayed systems cannot satisfy the increased demands, but plasma sprayed continuously graded coatings show improved performance and greater coating durability.

In addition to the flame spraying of thermal barrier coatings wear resistant coatings (molybdenum or steel) are sprayed by this technique. Characteristical structure of a molybdenum coating produced by flame spraying is shown in Figure 2. The microsection shows an inhomogeneous structure with few, small oxides, which exhibits many short, non-joined cracks [3]. Properties of flame sprayed molybdenum coatings are conditioned by the spray parameters. Differences in micro-hardness of about 800 Vickers units can occur due to different spraying conditions. Flame sprayed molybdenum coatings are suitable even for high specific loads, Fig. 3.

Steel coatings are produced by flame spraying too, in particular wear resistent coatings (13 % Cr-steel). The coating hardness is approximately HRc = 33 [5].

Sprayed coatings are also used as abradable seals [6]. Materials such as Ni-Al composite powder or nickel-graphite (75 % Ni / 25 % C) have been sprayed to produce satisfactory coatings as abradable seals. These materials tend to give better coatings by flame spraying than by plasma spraying because of the lower density attained by the former process [6]. Table 1 shows a synoptic table of the materials used for abradable seals.

## 3.2 ELECTRIC ARC SPRAYING

### 3.2.1 PRINCIPLE OF THE ELECTRIC ARC SPRAYING PROCESS

In electric arc spraying, two wires are passed through two electrodes, with a dc potential between them. Arcing occurs at the wire tips, producing high temperatures and the melting of wires. Molten particles are then accelerated onto the substrate by the compressed air stream, Fig. 4.

### 3.2.2 COATING PROPERTIES

The wire materials used in this process are often similar to those used in the wire flame spraying process. However, differences will exist in the resultant coatings, due to the different heating processes involved. For example, initial particle temperatures tend to be higher with this process.

The arc spray process is particularly well suited for high speed deposition of relatively thick coatings upon large components. This is mainly due to the high deposit rates, which in turn result from a very efficient method of melting the wire.

The possibilities of the arc spraying process have grown greatly in the course of application. As in the case of flame spraying, prior treatment of the parent metal surface is indispensable to achieve a good bond, but in addition to mechanical and physical adhesion, metallurgical interactions take place even when spraying aluminium onto steel. In many other cases some local welding has been shown to exist.

The adhesion under comparable conditions is higher than that with flame sprayed coatings; for example, the bond strength of mild steel was 30 N/mm² compared with 20 N/mm². The comparative average particle velocities, however, are 100 and 180 m/sec respectively, the arc spraying velocity being lower than that of flame spraying [7]. On the other hand, the particle size is greater and the temperature is higher, both factors being the cause of local welding. At the same time the shrinkage strains within the coating increase, so that any addition of heat input is to be avoided. A much higher burn-out of some alloying constituents will be a disadvantage as compared with flame spraying.

Arc length, current and voltage as well as wire feed speed and droplet size are different from comparative values in welding. The injected compressed air will cause disturbing effects and the arc will be quasi-stationary for a short time only.

The included angle between the electrodes varies from 30 ° to 60 °, and the arc ignition is by short circuit. Metal vapours and ionised gases are quickly generated and the boiling-point of most metals is soon reached. The losses, however may be kept low due to retardation of boiling with the oxides having a higher boiling temperature.

Considerable quantities of carbon are burnt out to steel wires, and a loss of manganese and silicon may be expected as a protective gas is not used for particle transfer in industrial applications.

The high temperature attained by a high arc current may be significant for all metallurgical phenomena in the arc area. According to spectrographic measurements, a temperature of 6100 ± 200 K is attainable in an arc between iron electrodes with a current of 280 amps, and it might be expected that similar conditions apply in the arc spraying of steel [7].

This process may be used too, to produce coatings of mixed metals, often termed 'pseudo alloys'. This may be achieved by feeding different wires through each electrode. For example, pseudo alloys of copper and stainless steel may be produced, resulting in higher wear resistance due to the steel, and a higher thermal conductivity due to the presence of copper.

## 3.3 PLASMA SPRAYING (ATMOSPHERIC)

### 3.3.1 PRINCIPLE OF THE PLASMA SPRAYING PROCESS

Figure 5 shows a schematic section through a plasma arc spraying head. In this process, a dc electric arc is struck between the nozzle and electrode, whilst a stream of mixed gases is passed through this arc. This results in dissociation and ionization of the gases, thereby producing a high temperature plasma stream from the gun nozzle. This plasma flame is capable of producing temperatures up to approximately 16.000 °C, although in practice most coatings will be deposited with a flame temperature in the range of 6.000 to 11.000 °C. Thus the process is apt to considerably increase the range of materials that may be used to produce coatings.

The system utilizes powder materials to be deposited, fed into the plasma flame from a powder port. The powder is suspended into a carrier gas stream, which will be of inert gas, usually argon or nitrogen. Both gases would normally be accompanied by hydrogen in order to increase power level. As a recent development, the use of argon/helium mixtures at increased gas flows will result in substantially higher particle velocities.

### 3.3.2 COATING PROPERTIES

By plasma flame spraying, coatings are produced which without any subsequent treatment are extremely dense, and well bonded to the substrate. Plasma coatings are more expensive to deposit than those of other processes discussed, and are used wherever their technical benefits will justify their increased costs.

Plasma coatings offer technical advantages over combustion coatings for the following reasons:

a) High particle velocities result in higher bond strength coupled with higher coating density.

b) A more efficient heat source results from the fact that a plasma, due to dissociation and ionization is at a very high energy level (often reffered to as the fourth state of matter). For this reason, heat energy is given up to powder particles accompanied by a minimum temperature drop in the surrounding gas stream, thus providing rather efficient particle heating. It makes lower particle 'dwell time' permissable, thereby reducing oxidation of particles.

c) The heat source is inert, thereby minimizing oxidation.

d) Higher plasma temperatures permit the spraying of materials with a higher melting point.

Due to the properties of the plasma flame, almost all materials can be sprayed provided they don't sublime or decompose at spray temperatures, for example silicon carbide, graphite and boron nitride.

Besides the high melting metals, oxides and carbides, materials with a very low melting point (even plastics) can be plasma sprayed. The variety of such materials may be taken from Table 2. Table 3 contains the most important properties of customary spray materials, and Table 4 provides a survey of properties and typical applications of plasma sprayed coatings.

## 3.4 LOW PRESSURE PLASMA SPRAYING (LPPS)

### 3.4.1 GENERAL REMARKS

The quality of the coating attained and the potential of the various spraying methods do not, however, always satisfy the demands made upon them. In this respect, the frequent occurrence of a porous coating structure or unsatisfactory adhesion can be regarded as disadvantageous. Moreover, reactive materials cannot be sprayed in the open air, and oftentimes coatings consistency with regard to thickness and chemical composition turn out to be beside the purpose.

Since both adhesive strength and homogeneity of coatings may be improved by increased particle velocity, high performance plasma spray guns have been developed in the past few years. In those cases, particle velocities are said to reach values of about 600 m/sec by means of a gas jet. As a consequence of the extremely short lingering time of the particles in the plasma, arc power of about 80 kW is required in order to melt the particles. This so-called "high energy" plasma spraying process is the latest state of technology and permits the fabrication of coatings with a high degree of density and good adhesion. The disadvantages named with spraying in the air, persist as before, however, and gas jet speed as well as particle velocity cannot be increased without incurring inproportionate costs.

However, if the entire plasma spraying process is displaced into low-pressure atmosphere, advantages arise which open up completely new fields of application for thermal spraying techniques. In particular, in a low-pressure atmosphere, particle velocity can be increased, and any harmful gas-metal reactions may be avoided. Thus coatings of high quality and chemical purity may be produced.

### 3.4.2 PRINCIPLE OF THE LPPS-PROCESS

Fig. 6 shows a system arrangement of the low pressure plasma spraying facility. The water-cooled chamber is evacuated by means of a pump to 0,3 mbar before spraying. During the spraying process, the pump maintains a pressure of approx. 70 mbar. A filter system and a heat exchanger are used to clean and cool the gas, loaden with the spraying material. Beside the main power sources, an additional source is necessary for the transferred arc.

Under pressure, the powder is transported to heating coils ahead of the plasma gun, where it is then injected into the nozzle of the gun.

The movement of both the gun and the sample is controlled by a preselection control system. Other details are comparable to atmospheric pressure plasma spraying facilities.

### 3.4.3 BASIC ASPECTS OF SPRAYING IN A LOW-PRESSURE ATMOSPHERE

#### 3.4.3.1 FORMATION OF THE PLASMA JET

The pressure conditions in the working chamber (50 to 70 mbar) accounts for the considerable increase in the plasma jet size, Fig. 7. In normal atmosphere, the plasma jet attains a length of 4 to 5 cm, whereas 40 to 50 cm may be achieved by spraying in a low-pressure atmosphere. This enlargement of the plasma jet has both advantages and disadvantages. The surface area of the base material is increased, and small variations in spraying distance exert no distinct influence on the coating quality. On the other hand higher powder losses and a lower energy density of the plasma jet in a low-pressure atmosphere must be regarded as unavoidable.

Due to the low pressure in the working chamber, the plasma gas jet velocity can also be increased up to three times the speed of sound, which means that the material being sprayed is also discharged at a higher velocity. Particles with a high degree of kinetic energy bring about good adhesion and few pores. However, since the particles linger for only a short time in the plasma, considerable electric energy is required for complete melting. This type of unit is thus designed for arc powers of up to 120 kW in order to be able to spray materials with a high melting point.

Additional energy can also be supplied by transferred arc between the nozzle of spray gun and the workpiece.

5.4.5.2 SPRAYING WITH TRANSFERRED ARC

If a voltage is passed between the nozzle and the workpiece, a discharge column is formed with a two-dimensional rather than punctiform end point, Fig. 8. This discharge column - the so-called transferred arc - has the following functions:

- intensive and rapid preheating of the workpiece
- cleaning of the surface to be coated
- supply of additional energy for melting the particles.

Preheating the Workpiece

For certain coatings the preheating of the workpiece is important, e. g. coating turbine blades. Heating up the surface to be coated with the plasma jet itself is too time consuming and expensive. If the preheating is done with an additional transferred arc, the required temperature can be reached quickly, Fig. 9. It can be seen that the sample used in the experiment (100 x 100 x 10 $mm^3$) was heated up to 600 °C in 48 seconds by using the transferred arc, whilst preheating by means of the plasma jet alone took 100 seconds. The amount of energy thereby required for the transferred arc is relatively small (6.75 kW).

Furthermore, the poling of the workpiece is critical for the preheating process. If the workpiece has a positive potential in relation to the nozzle of the plasma gun, there is a risk that thin oxide films (oxygen from plasma gases) form on the surface to be coated. These then inhibit adhesion to the substrate. Thus, in order to achieve optimum adhesion, it is recommended that preheating takes place with a negatively poled workpiece.

Cleaning the Surface to Be Coated

Mechanical clamping, physical adhesion, chemisorption and epitaxy, as well as metallurgical interaction can be regarded as decisive adhesion mechanisms for thermal spraying [11]. With the exception of mechanical clamping, the mechanisms presuppose active surface areas; the latter can be achieved by removing deposits of foreign substances. Deposits such as oxide, grease and dirt inhibit or prevent adhesion of the coating to the substrate. With conventional thermal spraying, the surfaces to be coated must be degreased and mechanically roughened immediately before spraying. In addition, roughening gives rise to latticing which promotes metallurgical interaction (diffusion). However, reoxidization of the surface before spraying cannot be prevented, in which case the wetting process is impeded. Oxide films are particularly likely to form when the workpiece is being preheated.

Plasma spraying in a low-pressure atmosphere offers the technological possibility of spraying on oxide-free surfaces with high surface energy, which leads to high adhesive factors. Spraying with a transferred arc (workpiece negatively poled) is of special importance. If during preheating the workpiece has a negative potential relative to the nozzle of the plasma gun, the electrons from the surface of the workpiece clean the surface to be coated. It can be assumed that disruptive adsorption or reaction layers will be completely eliminated and reformation of such layers, e. g. by reason of impurities in the plasma gas, will be prevented. The molten particles then encounter at a high speed surfaces with a high degree of cleanliness and surface energy, in which case favourable conditions are created for processes such as physical adhesion, chemisorption and epitaxy as well as metallurgical interactions. The "mechanical clamping" adhesion mechanism in this respect loses some of its relevance, as has already been proved by means of experiments. With the aid of a microprobe, increased diffusion can be detected, Fig. 10 b. When spraying takes place directlx onto the cold, grit blasted substrate, only slight diffusion is detectable, Fig. 10 a. A diffusion zone (titanium) of 7 µm can be established in the non-preheated and cleaned test sample compared with 11 µm in a test sample preheated and cleaned by the transferred arc.

However, in the evaluation of the concentration levels measured with the microprobe, the restrictions applicable to thermally sprayed coatings must be taken into consideration. In this respect, the lack of a definite reference level is a disadvantage, since the spraying is carried out on intensely roughened substrates. Only a few µm below the polished surface subjected to the electron beam, a completely different interfacial geometry can predominate, which leads to a distortion of the readings.

Unter certain conditions, mechanically roughening as a pretreatment of surfaces can be omitted. This fact has considerable relevance particularly for structural components exposed to high dynamic stress.

Supply of Additional Energy

The employment of a transferred arc for coating (workpiece (+) poling) is of importance for materials with super-high melting points. However, the transferred arc used during spraying gives rise to increased porosity in the case of some materials, e. g. titanium, which can be traced back to overheating of the material.

### 3.4.3.3 GAS-METAL-REACTIONS

Gas-metal reactions, such as alloy burn-off oxidation and nitride formation can only be caused by impurities in the plasma gases, by residual oxygen or nitrogen in the working chamber or by contaminated spraying powder.

The inert plasma gases will not cause such reactions. In order to reduce the reactions as far as possible, the spraying process must be carried out with secondary-cleaned gases (purity over 99.997 %) as well as with low-oxygen-powders. Moreover, the working chamber must be evacuated to 0.2 - 0.3 mbar before starting the spraying process.

If these regulations are observed, even reactive materials can be successfully sprayed, since the remaining impurities should be of no consequence for most of the applications. The same applies to coatings whose purpose is to protect the base material from oxidation during its subsequent working life. Since this can only be achieved when the oxygen is prevented from diffusing in from the outside, premature oxidation of these metals during spraying must be prevented. Examples of this kind of coating, which are already being applied with success by means of low-pressure plasma spraying, are coatings on Co(Ni) CrAlY-basis which are resistant to hot gas corrosion.

## 3.4.4 COATINGS APPLIED BY MEANS OF LOW PRESSURE PLASMA SPRAYING

### 3.4.4.1 MO/$MO_2C$-COATINGS

Plasma-sprayed Mo/$Mo_2C$-coatings are expected to exhibit great resistance to wear with reduced sliding friction. The molybdenum thereby serves as a ductile matrix material, whilst an increased wear resistance is obtained through the $Mo_2C$ (HV 0.025 = 1950). The constitutional diagram C-Mo, Fig. 11, may give an indication of the difficulties created by the spraying of these materials. Thus, in the case of atmospheric spraying, a high carbon oxidizing loss can be anticipated, which can lead to a substantial decrease in the $Mo_2C$ content. On the other hand, the molybdenum loses some of its ductility through solid solution and precipitation hardening as a result of reaction with the oxygen in the air. Atmospheric spraying thus turns out to be unsuitable.

For this reason it is appropriate to spray this combination of materials in an inert atmosphere, since oxidizing losses are prevented to a large extent and the ductility of the molybdenum is maintained.

In Fig. 12 the transverse micro-sections of Mo/$Mo_2C$-coatings (50/50) sprayed in a low-pressure atmosphere and in a normal atmosphere are shown in comparison. The micro-section in Fig. 12 a (sprayed in a low-pressure atmosphere) enables three different phases to be recognized, which can be identified as $Mo_2C$ (HV 0.025 = 1600), molybdenum (HV 0.025 = 291) and an eutectic constituent of molybdenum and $Mo_2C$ (HV 0.025 = 561). In Fig. 12 b the structure typical for atmospherically sprayed molybdenum coatings predominates;pure molybdenum particles cannot be identified;molybdenum carbide only sporadically. Chemical analysis establish the high lost of carbon due to atmospheric plasma spraying, Table 5.

<u>Effect of Transferred Arc</u>

The metallographic investigations give no indication of the effect of the transferred arc, which is switched on during the coating procedure. Neither positive nor negative effects of the transferred arc in the course of preheating and/or cleaning the substrate are to be determined on the basis of the transverse micro-section. Mechanical-technological tests on the coatings, however, demonstrate that transferred arc is apt to improve adhesion as well as cohesion of the coating. As a result, by means of bending and indentation test it was demonstrated that coatings sprayed on samples not even subjected to grit blasting treatment exhibited good adhesive qualities as long as the transferred arc was used for spraying, Figs. 13 and 14. Coatings sprayed with the transferred arc onto surfaces not subjected to grit blasting treatment exhibit better adhesion that those sprayed without transferred arc. The assumption that roughening of the surfaces is not exclusively required, is thus confirmed by the experiments. The adhesive strength values enter an order of magnitude which is out of range of the test method according to DIN 50 160 since existing adhesives are not capable of adhesive strengths of 70 $N/mm^2$ and more.

### 3.4.4.2 COPPER-, CHROMIUM- AND MCRALY-COATINGS

As mentioned above, protective hot gas corrosion MCrAlY-coatings can be produced by low pressure plasma spraying. The transverse micro-section of such a coating is shown in Fig. 15. The coating structure is free of oxides and nearly free of pores. These are essential preconditions for successful application in gas turbines.

A pure copper-coating sprayed under comparable conditions exhibits a similar favourable structure, Fig. 16.

Fig. 17 shows a comparison of chromium-coatings sprayed in different atmospheres. Whilst the coating sprayed under atmospheric conditions has a porous structure with oxides and inclusions, an oxide-free coating with insignificant porosity can be detected

from LPPS. It can be assumed that these coatings are corrosion resistant.

### 3.4.5 CONCLUDING REMARKS

The results achieved until now show that, with the aid of low-pressure plasma spraying, complicated material systems can successfully be sprayed. Taking a mixture of $Mo/Mo_2C$ as an example, it was shown how carbides can be sprayed without any problem. The resulting coating is composed of a ductile molybdenum matrix, the eutectic alloy $Mo/Mo_2C$ and pure $Mo_2C$. Increased adhesive bond strength of the coating can be achieved by means of an additional transferred arc, with good adhesion being obtained even on the surfaces which have not been roughened. Wear tests will have to prove the suitability of the coating under operating conditions.

In conclusion, high-energy, low-pressure plasma spraying opens up new fields of application for thermal spraying. However, great efforts must be taken to introduce this process into industrial practice.

## 3.5 DETONATION GUN TECHNIQUE

### 3.5.1 PRINCIPLE OF OPERATION

The detonation gun equipment is housed in a double-walled, soundproof cubicle and remotely controlled from outside by an operator at a consul [13]. Using the diagrammatic view of the gun shown in Fig.18, a complete cycle of one detonation can be considered. Accurately metered quantities of oxygen and acetylene are fed, via the poppet valves, into the combustion chamber. Powder, in a nitrogen carrier gas stream, is accurately metered from a heated, pressurised dispenser and is suspended in the gas mixture within the barrel. At the same time, nitrogen from a separate source is metered into the combustion chamber to surround the poppet valves and protect them from hot gas erosion following detonation. When all the valves are closed, the gas mixture is ignited by a spark plug, fed from a magneto which is synchronized with the gas flow poppet valve system. The detonation or shock wave which follows within milliseconds after ignition, attains a velocity of about 3000 m/s [13]. Another author gives a speed of approximately 3900 m/s of the moving wave front [14].

The detonation wave, followed by a rapid expansion of the reacted gas products, accelerates the powder particles so that they leave the open end of the barrel at about 750 m/s. The actual particle velocity reached will depend on a number of factors: i. e. chemical gas mixture, ratio of gaseous mixture, barrel length, size of powder particle and position of suspended powder prior to detonation. The coating powder particles are heated up by the hot gas stream and most materials are melted. The cycle is completed with the nitrogen valve opening and a purge stream sweeping out the gaseous products of combustion.

Depending on the type of coating applied, this cycle is repeated 4.3 or 8.6 times per second. This produces a coating structure which is built up of a series of detonations or 'pops' on the prepared substrate placed in front of the barrel.

The molten particles leaving the gun barrel at high velocity produce a high density layer on impact. The high kinetic energy of the particles is approximately twentyfive times that of the energy in particles produced by flame spraying process. On successive detonations, build-up of coating recurs to the desired thickness, usually between 0,05 and 0,4 mm [13].

### 3.5.2 COATING PROPERTIES

The hardness of detonation gun coatings is generally higher than that of equivalent coatings produced by the other two flame spraying techniques. This is basically due to the very dense structure achieved by the high impact velocity of the process. The typical hardness for a tungsten carbide/cobalt detonation-gun coating is 1300 V.P.N.(Vickers Pyramid Number). The hardness of similar coatings produced by plasma spraying would be of the order of 600 - 800 V.P.N. Those of coatings produced by combustion spraying would be still lower [13].

The porosity of detonation-gun coatings is very fine, normally of about ten microns in diameter. The overall amount is usually between 1/4 - 1 % and this is evenly distributed. This low level of porosity can be compared to values of several per cent for most plasma-sprayed coatings and even higher levels of porosity for combustion-sprayed coatings. Advanced plasma torches are now able to apply certain coatings which have porosity levels close to those of detonation-gun coatings.

The bond strengths of detonation-gun coatings to their substrates are extremely high. In general, bond strengths greater than 85 $N/mm^2$ have been measured and in certain instances bond strengths of 176 $N/mm^2$ have been recorded. The bond strengths of plasma coatings are less due to the lower particle impact velocity of the plasma process. The range of bond strengths of plasma coatings is 21 - 85 $N/mm^2$ - depending greatly on the type of plasma equipment used. The combustion-spraying process generally requires the use of a bond coat, so that the bond strength measured is really that of the bond coat which can be as high

as 21 N/mm$^2$ [13].

Examination of the microstructure of detonation-gun coatings shows a very dense laminar structure. The microstructure of plasma-sprayed coating is more porous and of a more turbulent appearance. Combustion sprayed coatings offer a greater amount of porosity and many round particles, which were not molten on impact, trapped in their structure.

Table 6 gives a survey of typical detonation-gun coatings and coating propertis.

## 4. QUALITY CONTROL

### 4.1 PRESENT STATUS

Quality in sprayed coatings stems from good process control at every stage of the processing cycle [15]. A variety of tests is used to establish the quality of a deposit. When destructive tests are used, they should be performed on test pieces. The problem is to ensure that the spraying conditions used on the component are substantially the same as those of the test coupon [15]. Suitable destructive tests are metallographic examinations, hardness tests and estimation of coating adhesion and tensile strength. Application of non-destructive test methods is very difficult owing to inhomogeneous structure of the coatings. Worldwide there are many efforts to develop applicable non-destructive methods to test sprayed coatings. The following chapter gives a report of recent investigations carried out at Dortmund University.

### 4.2 NON-DESTRUCTIVE TESTING OF THERMALLY SPRAYED COATINGS

#### 4.2.1 THERMOGRAPHY

Thermography determines the temperature distribution on surfaces by an infrared image.

This procedure is also adopted for non-destructive materials testing. Thus, in the literature examples for the application of the procedure for detecting cracks and pores in welded joints and defects in adhesive bonded joints are reported [16, 17].

A prerequisite for the application of this method is that the sample is heated up to a moderate temperature. Measurements are made either when the maximum temperature has been reached (static thermal test method) or in the heating-up and cooling-down phase (dynamic).

Inhomogeneities such as bonding flaws show up as disturbances in the heat flow. Heat may either accumulate or be prevented from flowing through the layer dependent on which part of the system had been heated up.

The results are local variations in surface temperature, which permit conclusions to be made regarding flaws in the coating or varying bonding properties.

This process is particularly suitable for materials with poor thermal conductivity, since in this case thermal equilibrium is reached relatively slowly.

Bucklow [18] and Nitsche [19] refer to the possibility of employing thermography for determining the bond strength and homogeneity of thermally sprayed coatings, although they do not supply any concrete results.

In order to determine the potential of the method, ceramic sprayed coatings were tested on a substrate with good conductivity.

The substrates (84 mm diameter, 10 mm thick) of mild steel were ground plane-parallel and after degreasing subjected to blasting at 2.5 bar. Several points on the relatively unroughened surfaces were then covered, and the whole surface subjected to blasting at 8 bar. In the course of the subsequent spraying process, this resulted in areas with insufficient bonding.

The temperature differences to be expected lie in the range of 0.2 $^{o}$C. Thus, homogeneous heating up is of major importance, otherwise the local differences in at supply will lead to temperature differences which are an obstacle to flaw finding.

For this reason, the heat is initially equalized by a copper cylinder (84 mm diameter, 10 mm high) before being passed onto the sample. The temperature field is then photographed by a thermocamera and displayed via monitor in black and white or in colour.

As may be pointed out by thermograms of the copper surface in the most sensitive range of the thermocamera, the necessary degree of homogeneity in temperature distribution or a reproducible symmetry in the heat supply could not be attained yet by means of the described heating arrangement, Fig.19. For this reason, flaw finding during the heating up phase, in which the local differences in heat

supply are maintained, was difficult. On the other hand, during cooling down it was possible to observe how temperature differences in the flawless zones are averaged faster than those between flawed and flawless zones. The best results were achieved during the cooling down process in the temperature interval 70° - 80°C after the test samples had been rapidly heated up to about 80 °C - 90 °C. Flaws then are exposed as deviations in a radial, symmetrical, isothermal field balanced for the main part, Figs. 20 and 21. In the selected vertical set-up of the samples in this range of sensitivity, the deeper and cooler parts of the sample do not appear on the monitor, Fig. 22. This problem can be resolved by positioning the samples horizontally. This arrangement does, however, necessitate a metal mirror to deflect the heat radiated from the sprayed coating into the thermocamera. In order to determine the detection potential, square bonding flaws of varying size were produced. The temperature image of this sample is to be seen in Fig. 22. Whilst the large square (6 mm side length) is easily recognizable, two smaller squares below left (3 mm side length) are less readily visible. Thus a flaw with a side length of 5 mm can be regarded as the smallest readily recognizable flaw size.

### 4.2.2 HOLOGRAPHIC INTERFEROMETRY

Optical holography is an interferometric process which in the past has been successfully adopted for detecting material flaws [20 - 22].

The object being tested is illuminated with laser light, and a hologram is produced. Subsequently the component is deformed and holographed once again. The measurement results are obtained as interference fringes which are superimposed on the object image.

Where flaws exist, the surrounding area shows relatively strong deformations. This enables flaws of even smaller dimensions to be perceived if they are near to the upper surface. The particular advantage of the method is that even surfaces of complicated geometry may be inspected in a single interferogram with the measurement not being distorted by the surface roughness.

For detecting flaws in sprayed coatings, three holographic methods can be recommended:

Deformation holography, contour holography and vibration holography in connection with ultrasonics.

Deformation holography detects the deformation of a surface. Since detaching can hardly be detected by subjecting the test sample to mechanical stress, the sample is heated up in a similar manner to that in thermography. The temperature increase is less than 20 °C. In the case of flawless samples, this results in a relatively homogeneous expansion, which is visible as parallel interference fringes. If flaws are present, the flaw zone becomes deformed differently to the flawless zones as a result of heat accumulation and different temperature expansion coefficients. This leads to characteristic changes in the interference pattern, Fig. 23.

The flaw in the centre of the test sample gives rise to a concentric system of fringes in the image, whilst the remainder of the sample is covered with straight fringes. This method is particularly suitable for detecting coating detachings. Hitherto, flaws with diameters as small as 10 mm have been detected.

In contrast to deformation holography, contour holography permits surface profiles (and thus variations in the thickness of coatings on components) to be measured.

In this manner the coating can be inspected for uniform thickness. Local variations in thickness, manifested in the form of arches or hollows, can be detected with particular ease. With this process the interference fringes are obtained either by slightly varying the angle of object illumination or by changing the wave length of the laser light. The component thus need not to be stressed.

In Fig. 24 relatively uniformly coated parts of the test sample are indicated by parallel, equidistant fringes. If the fringes vary either in their direction or their spacing, inhomogeneities in the thickness of the coating are present. In Fig. 24 this applies mainly to the peripheral zone of the sample. With the aid of a specially developed technique, deviations of approx. 30 µm can be detected on samples of up to 30 cm in size [23].

Whilst mainly qualitative information was hitherto gained from holographic interferograms, today there are computational methods which carry out a quantative evaluation [24].

Fig. 25 shows an unevenly coated sample with its interference fringes. The points which deviate more than the permissible degree (in this case more than 100 µm) are calculated automatically and displayed graphically, Fig. 26).

The third method, vibration holography, is also suitable for detecting small flaws when used in connection with ultrasonics.

The imaging of vibrations in the megahertz range, which are of particular interest for ultrasonic testing, is however difficult because of the smallness of the vibration amplitudes. Only with the aid of the so-called reference beam modulation [25] - which has to be modified in a special way - on the optical side, and simultaneous employment of the

CS technique on the acoustic side is it possible to make these ultrasonic fields visible on the hologram.

A wave field with a frequency of 1.5 MHz which has passed unobstructed through a steel test sample manifests itself in parallel, equidistant interference bands, Fig. 27. If the ultrasonic field is distorted by a 2 mm wide flaw (borehole), this can be recognized in the circular structure of the interference fringes, Fig. 28.

It must be pointed out that these results were gained at a relatively early stage of the experiments. The high level of resolution with a simultaneous clear margin of independence from the surface structure is encouraging.

### 4.2.3 ULTRASONIC TESTING

Ultrasonic techniques offer the greatest potential for transferring research achievements into practice.

The ultrasonic testing experiments hitherto conducted on sprayed coatings produced some very promising results [26], although these do not appear to be transposabel to other spraying methods, spraying parameters and coating qualities. In particular, the experience won with regard to resolution, defect identification and the influence of test frequency on flaw and scattering readings now enable intensive application of ultrasonics and their different wave types.

For this purpose the so-called "CS-technique" (Controlled Signals) appears to be most suitable [27 - 29], which has greater regard for the frequency-dependent parameters of ultrasonic wave propagation.

Besides the detection of flaws the determination of the coating structure is expected to be possible.

The dimensions of the samples used in the ultrasonic test experiments are shown in Fig. 29. The arc-sprayed coating of carbon steel had a thickness of about 1.8 mm, whilst the base material was of mild steel. The following two flaw types were incorporated in the samples, each of them being represented in two different dimensions (7 and 14 mm):

a) Bonding flaws (interface not sand-blasted)

b) Pore clusters or detachments of coating (spraying with a mask in front of the sample).

The simplest method of detecting bonding flaws is the analysis of the backwall echo by insonification from the sprayed side. This makes use of the fact that the height of the backwall echo, which passes twice through the interface when using a pulse technique, is dependent on the discontinuity in impedance from the sprayed coating to the base material. If bonding flaws do exist, this discontinuity in impedance can be expected to be substantially larger than in the case of a flawless bonding, so that the backwall echo showed drop clearly in the case of deficient bonding. The line scans (immersion method) shown in Fig.30 confirm this assumption; bonding flaws can easily be detected by the weakening of the backwall echo.

Flaw readings thereby depend on frequency with the detection sensitivity decreasing slightly as the frequency increases. Since initially, besides the divergence losses, no frequency dependence is to be expected in the case of vertical reflection on an interface, only the influence of sound scattering in the sprayed coating and of interference remains to be considered. However, because this influence is minimal and hardly obstructs the detection of flaws, it can be neglected for the time being.

In practice, this gives rise to additional difficulties, as frequently components do not give backwall echoes capable of being analysed (e. g. complicated geometries). In this case other test methods must be employed. Judging by the first experimental results available, the CS technique using AE transducers appears to be successful. The sound passage through a sprayed coating on employing an AE transducer is schematically shown in Fig. 31. If the bonding between the substrate and the sprayed coating is satisfactory (small impedance discontinuity) the ultrasonic waves will be reflected at the interface to a minor extent only. The echo received then exhibits a minor amplitude. However, if there is a bonding flaw with a stronger impedance discontinuity under the transducer, the interface echo will be intensified.

With the angular reflection within the interface, mode conversions occur. These are not accounted for in the schematic view, although they have an effect on the test results. In addition, distinctive interference phenomena can be expected in the course of the sound wave propagation in the sprayed coating (impulse length / coating thickness), which depend on the test frequency and the thickness of the coating, whilst they are subject to the influence of the vibrational state of the coating at the same time.

This is confirmed by a comparison of the spectra of two sets of readings from a flawed and a flawless zone; both spectra exhibit distinctive interruptions (interference effects), which are, however, shifted to lower frequencies in the case of the flawed zone than the flawless zone. With a test frequency of about 2.6 MHz the spectrum of the flaw-

less zone has a minimum, whilst the bonding flaw has a maximum value at this point. This frequency range can be exploited in a well defined way, Fig. 32. According to the spectroscopic results in Fig. 33, measurements in the range of approx. 2.7 MHz give the best signal/noise ratio. The reading at 300 mm is caused by an unintentional natural flaw. Towards the higher and lower frequency ranges the detection sensitivity deteriorates. The two measuring methods described are capable of detecting bonding flaws in a distinctive manner, but they have hitherto failed to detect pore clusters. This test shortcoming can, however, be remedied by employing special types of wave, such as surface waves.

In this case, detection of an extremely porous zone of 14 mm in diameter by excitation of surface waves with CS technique is shown in Fig. 34. Using a test frequency of 1.62 MHz, the detection of flaws is most distinctive with about 20 dB above the noise level. An increase or decrease of the centre frequency of the pulses results in a substantial decrease in the flaw echo.

The cause of this strong dependence on frequency is not yet fully clarified. The pores are, however, only slightly larger than large drops in the coating. For this reason, extremely high scattering readings can be expected from the porous coating, the frequency dependence of which, however, differs from that of the reflectors. Moreover, guided waves appear in thin layers whose excitation is strongly dependent on frequency.

### 4.2.4 ACOUSTIC EMISSION ANALYSIS

In comparison to the active test methods described above, passive acoustic emission analysis lends itself particularly well to supervisory functions. Its potential for detecting phase transformations, crack initiation and crack propagation, plastic deformation and frictional processes resulted in the employment of acoustic emission analysis for thermal spraying. Particularly efficient detection of cracks and detachings of the coating may therefore be anticipated.

In as far as it is possible to draw a correlation between the spraying parameters and acoustic emission signals emitted during the cooling down of the coating, a direct relationship between signals and coating characteristics appears likely on the basis of existing and sufficiently known interdependences between spraying parameters and mechanical-technological characteristics.

The various parameters (current intensity and air pressure for arc spraying, also the preheating temperature of the substrate for flame-spraying) have a very distinct effect on the sound emitted during the cooling process, Figs. 35 to 37. Thus the total number of counts rises with increasing current intensity. This is attributed to the increased heat supply and associated greater stresses. The reduction of these manifests itself in a higher level of acoustic emissions during the cooling down phase by plastic deformation and microcracks.

A high level of acoustic emissions can also be obtained by reducing the air pressure, Fig. 36. The reason for this is also seen in the increased heat supply. When spraying with low pressure, comparatively large particles are formed, which during their flight do not cool down as much as small ones. As a coating of larger, hot particles on a cold substrate cools down, more pronounced deformation occurs than in the case of coatings composed of smaller, already cooled particles.

Acoustic emission also attributable to differing shrinkage processes can be observed in flame spraying on various preheated substrates, Fig. 37. Because the deformation difference is greater in the case of old substrates, higher levels of sound emission occur here.

A further advantage of sound emission as a means of monitoring is that the beginning of failure processes under load is indicated. In this way, determination of the risk of flaws is possible: for this purpose, coated samples (400 x 5 $mm^2$) were bent. If the bending took place within the elastic range, hardly any sounds were emitted, providing the sample was flawless. Immediately after departing from the elastic range there was a huge increase in acoustic emission, which was attributable to beginning deformation and in particular crack formation within the coating. Plastic deformation in the base material was not detected, as was demonstrated by comparitive measurements on uncoated samples, Fig. 38.

Metallographical investigations on loaded samples show up these cracks, Fig. 39. They run along the oxides which form the weak points within these coatings. The first microscopic damages can thus be correlated directly with high acoustic emission. Flawed samples emit increased acoustic emission already at stress levels which are within the elastic range of flawless samples, by which means one can distinguish between flawless and flawed samples.

## 4.3 CONCLUSIONS

The alternatives for non-destructive testing of sprayed coatings have been introduced and discussed. The most promising test methods prove to be ultrasonic testing, optical holography, thermography and acoustic emission analysis. Those methods were in-

vestigated on specimens with model flaws and the results were discussed. In particular, the ultrasonic technique employing controlled signals (CS-technique) is able to bridge the wide gap hitherto existing in the testing of sprayed coatings, with guaranteed reproducibility of the results.

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## 5. REFERENCES

/ 1 / Saywell, W. A.: Flame Sprayed Coatings, Electroplating and Metal Finishing
December 1973, pp 12 - 16

/ 2 / Wilkins, C. R., F. J. Wallace and P. H. Zajchowski: Ceramic/Metallic Thermal Barrier Coatings for Gas Turbine Engines
8th Int. Thermal Spraying Conference, Miami 1976

/ 3 / Steffens, H.-D.: Thermisch gespritzte Metallschichten zur Verminderung von Reibung und Verschleiß
VDI-Berichte Nr. 333, 1979, S. 105 - 111

/ 4 / Beyer, H.: Entwicklung verschleißfester thermischer Oberflächenschichten
Metalloberfläche 29 (1975), Heft 10, S. 512 - 516

/ 5 / Gagnet, W. J.: Flame Spray Coating for Wear
Society of Automotive Engineers, Mid-Year-Meeting, Chicago May 19 - 23, 1969

/ 6 / Messbacher, A.: Thermisches Spritzen im Flugtriebwerkbau
wt-Z. ind. Fertig. 65 (1975), S. 619 - 624

/ 7 / Steffens, H.-D.: Fundamentals of Arc Spraying, in: Metal Spraying by the Electric Arc
Seminar Handbook, The Welding Institute 1973

/ 8 / Solomir, J. G.: Plasmaspritzen - Bau, Funktion und Anwendung der Spritzanlagen
Technische Rundschau Nr. 28, 1970

/ 9 / Gerdemann, D. A. and N. L. Hecht: Arc Plasma Technology in Materials Science
Springer Verlag 1972

/ 10 / Meckelburg, E.: Metall-Spritzverfahren - unbegrenzte Möglichkeiten (Teil 1), Fachberichte für Oberflächentechnik 10 (1972), H. 5, S. 179 - 184

/ 11 / Steffens, H.-D. und K.-N. Müller: Grundlagen der Haftung thermisch gespritzter Schichten
Adhäsion (1972), Heft 2, S. 34 - 38

/ 12 / Hansen, M. und K. Anderko: Constitution of binary alloys
Mc Graw-Hill Inc., New York, 1958

/ 13 / Cashon, E. P.: Wear Resistant Coatings Applied by the Detonation Gun
Tribology international June 1975, pp 111 - 115

/ 14 / Cook, E. B.: Coating Developments for the Gas Turbine Hot Section

Thirteenth Airlines Plating Forum, Dallas, Texas February 1 - 3, 1977

/ 15 / Smart, R. F.: Quality Control of Sprayed Coatings

8th Int. Thermal Spraying Conference, Miami 1976

/ 16 / Kopineck, H. J. Thermische Prüfverfahren

Neuzeitliche Verfahren der Werkstoffprüfung, p. 162-184, Verlag Stahleisen, Düsseldorf (1973)

/ 17 / N. N.: Anwendungsbeispiele der Infrarot-Thermographie in der NDT

MBB WF Information, 2, p. 23 - 32 (1979)

/ 18 / Bucklow, I. A.: Possible methods for NDT of sprayed coatings

Advances in Surface Coating Technology, Conference, London (1978)

/ 19 / Nitsche, K.: Schichtmeßtechnik

VEB Verlag für Grundstoffindustrie, Leipzig, 1. Auflage

/ 20 / Stetson, K. A. and R. L. Powell: J. Opt. Soc. Am. 56, 9 (1966)

/ 21 / Harris, W. J. and F. C. Clauss: Inspecting bonded structures by laser holography

Metal Progress, 8 (1971)

/ 22 / Grünewald, K.: Holographisch-Interferometrische Untersuchungen an GFK und KFK-Bauteilen

Z. f. Werkstofftechnik, 3 (1974)

/ 23 / Kreitlow, W. and W. R. Fischer: Final Report of the DFG Research Project Mi 80 / 40

/ 24 / Fischer, W. R., H.-A. Crostack and H.-D. Steffens: Automatic analysis of holographical interferograms for non-destructive testing

Paper at Laser-Opto-Electronic 1979, Conference, Munich, 1979

/ 25 / Aleksoff, A.: Time average holography extended

Applied Phys. Lett., Vol. 14 (1969)

/ 26 / Francke, W. and A. W. J. de Gee: A non-destructive method for the adhesive bond strength of thermally sprayed nonfused coatings

Advances in Surface Coating Technology, Conference, London, 1978

/ 27 / Crostack, H.-A. et. al.: Ultraschallprüfung mit Sendeimpulsen stufenlos veränderlicher Frequenz und steuerbarer Spektralverteilung

Materialprüfung 20, Vol. 10 (1978)

/ 28 / Crostack, H.-A. und H.-D. Steffens: Untersuchungen zur Steuerung von Ultraschallimpulsen und ihr Einsatz in der zerstörungsfreien Werkstoffprüfung

DGZfP-Conference Mainz (1978)

/ 29 / Crostack, H.-A.: Beitrag zur Verbesserung der Ultraschallprüfung beim Ermitteln von Fehlern in schwer prüfbaren Werkstücken

Inaugural Dissertation, Dortmund University (1978)

| Types of Materials Used | Operating Temperature (°C) | Hot Spraying Process |
|---|---|---|
| Aluminium-Silicon Alloy with Polyester | 350 | Flame Spraying |
| Aluminium | 400 | Plasma Spraying |
| Nickel 75 - Graphite 25 | 540 | Flame Spraying |
| Nickel 85 - Graphite 15 | 640 | |
| Nickel - Chromium - Boron Nitride | 700 | |
| Copper - Zinc - Silver | 350 | Flame Spraying |
| Nickel - Aluminium | 920 | |
| Nickel - Chromium - Aluminium | 950 | |

Table 1:

Materials used for abradable seals [6]

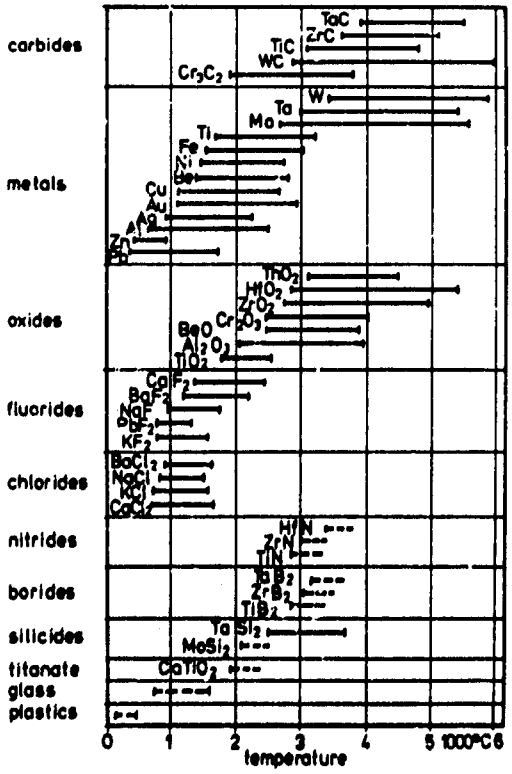



Table 2:

Survey of Plasma Spraying Materials [8] (Melting and Boiling Points)

Table 3: Properties of spray materials [9 and 10]

| material / property | metals | | | | oxides | | | | | | | | | carbide | | | | | borides | nitrides | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Be | Mo | NiAl | W | $Al_2O_3$ | $BaTiO_3$ | $CeO_2$ | $Cr_2O_3$ | $HfO_2$ | MgO | $TiO_2$ | $ZrO_2$ | $ZrSiO_4$ | CrC | HfC | TaC | ZrC | WC | $ZrB_2$ | TiN | ZrN |
| density, % of theoretical density | 85-90 | 88-93 | 85-95 | 80-93 | 85-91 | 80-90 | 92 | 90-95 | 87 | 90-95 | 70-85 | 85-95 | 85-90 | 96-97 | 81-87 | - | - | 90 | 93 | - | - |
| melting point °C | 1280 | 2620 | - | 3410 | 1980-2040 | 1610 | 2600 | 1650 | - | 1930 | 1760 | 2480-2580 | 1650 | 2040 | 3890 | 3880 | 3540 | 2870 | 2990 | 2950 | 2980 |
| specific heat kJ/kgK | - | - | - | - | 1,26 | - | - | 0,84 | - | 1,05 | - | 0,71 | 0,63 | - | - | - | - | - | - | - | - |
| thermal conductivity W/mK | - | - | - | - | 1,73-2,88 | - | - | 2,60 | - | 2,60 | 2,16 | 0,58-1,15 | 2,16 | - | - | - | - | - | - | - | - |
| coefficient of thermal expansion $10^{-6}$ 1/K | - | 6,3 | - | 4,9 | 7,2-12,6 | - | - | 9,0 | - | 8,1 | 7,0 8,3 | 5,4-12,6 | 7,2 | - | 6,6 | 6,3 | 6,7 | - | 6,9 | 9,4 | 6,0 |
| tensile strength N/mm² | - | 28-173 | 35-41 | 69-145 | 21-83 | 166 | - | - | - | - | - | 7-10 | - | - | - | - | - | - | - | - | - |
| compressive strength N/mm² | 276 | - | - | - | 138-242 | - | - | 207 | - | - | - | 138-207 | - | 28-69 | 221-331 | 221-290 | 110 | - | 69 | 255 | 297 |
| elongation, % | - | 0,3 | - | - | 0,7 | - | - | - | - | - | - | 1,4 | - | - | - | - | - | - | - | - | - |
| breaking modulus N/mm² | - | 242 | - | 138 | - | - | 60 | - | - | - | - | 24 | - | - | - | - | - | - | - | - | - |
| modulus of elasticity $10^3$ N/mm² | 200 | 340 | - | 280-410 | 41 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| hardness HV 0,1 | - | 170 | - | 350 | ≈ 1000 | ≈ 730 | - | 1250-1470 | 250-310 | - | ≈ 850 | 600-800 | - | - | 400-800 | 300-1000 | 800 | - | 1000 | 780-1100 | 620 1120 |
| adhesive strength, N/mm² | 14-21 | 19 | 21-25 | 7 | 10 | 7 | - | - | - | - | - | 10-11 | 7-14 | - | - | - | - | 21 | - | - | - |
| emissivity | - | - | - | - | 0,8 (2000°C) 0,5 (760°C) 0,4 (980°C) | - | - | 0,9 (120°C) 0,75 (980°C) | - | - | | 0,7 (200°C) 0,8 (650°C) | - | - | - | - | - | - | - | - | - |
| disruptive strength kV/mm | - | - | - | - | 8 | 4-12 | - | - | - | - | - | 2-4 | - | - | - | - | - | - | - | - | - |

Table 4: Summary of coating application for plasma sprayed materials [9]

| Material | Melting Point (°C) | Possible Areas of Usefulness |
|---|---|---|
| Alumina 50 % Titania Blend | 1921 | Strongly adherent coating, temperature-resistant, moderate resistance to thermal shock (Maximum usable temperature is 1093°C in oxidizing atmosphere). |
| Alumina-40 % Nickel Blend | 1454 | High-temperature coatings where thermal shock is a problem. |
| Aluminium Oxide-Titania Trace | 1927 | Low-cost ceramic provides good temperature, wear and impact resistance. Low reaction to molten metals (Maximum usuable temperature 1538 °C oxidizing atmosphere). |
| Aluminium Oxide-Pure | 1982 | Good wear, heat and corrosion resistance, good insulator; stable in oxidizing or reducing atmosphere at 1538°C, resists product pickup on annealing-furnace rolls and has low reactivity to molten metals. Thermal-control coating. |
| Boron Carbide | 2430 | Cermet component, nuclear shielding and controlrod material; wear- and temperature-resistant. |
| Calcium Zirconium | 2343 | Thermal barrier coatings. Resistant to wetting by various metals, and can be used for coating melting pots and allied equipment. Dense, hard, abrasion-resistant coatings with very good bond. Maximum usable temperature 1315 °C in oxidizing atmosphere. |
| Ceric Oxide | 2600 | Thermal barriers, combustion catalyst. |
| Chromium | 1890 | Bearing surfaces at low to medium temperatures. Corrosion-resistant coatings when properly sealed. |
| Chromium Carbide | 2040 | Wear-resistant coatings, mixture with metal powders for cermet coatings and wear resistance at higher temperatures. |
| Chromium Carbide-40 % Cobalt Blend | 1480 | Wear-resistant coatings, particularly on aluminium and other non-ferrous metals where bond is excellent. |
| Cobalt | 1490 | Dense, strongly adherent coatings. Mixture with ceramics for cermets. |
| Magnesium Zirconate | 2110 | Thermal-barrier coatings, resistant to wetting by various metals, and can be used for coating melting pots and allied equipment. Especially useful in lining graphite crucibles used in melting and refining uranium. |
| Molybdenum | 2620 | Bonding metal and ceramic coatings for low-temperature use, hard wear-resistant surfaces. Also for electrical contacts. |
| Rare Earth Oxides | >2200 | Thermal barrier and combustion catalyst. Recommended for coating of diesel pistons and combustion chambers. Reduces fractures in combustion chamber. |
| Titanium Carbide | 3090 | Cermet component, high-temperature electrical conductor. Good thermal and oxidation resistance. (Maximum useful temperature 1370 °C in oxidizing atmosphere). |
| Titanium Oxide | 1920 | Hard, abrasion-resistant, minimum-porosity coatings with excellent adhesion to base. For mixture with other ceramic and metal powders to improve physical properties of the coatings. |
| Tungsten | 3410 | Liners for rocket-engine throats and tail cones. |
| Tungsten Carbide | 2870 | Excellent blast-erosion qualities as sprayed for high-temperature applications i. e. rocket nozzle coatings. Excellent abrasion resistance through temperature range up to 815 °C. |
| Tungsten Carbide-12 % Cobalt Blend | Softens at above 1490 | Good adherence with good wear and shock resistance. |
| Zirconia 40 % Cobalt Blend | above 1650 | High-temperature cermet coating. High hardness and abrasion resistance. Retards oxidation of base materials and has excellent thermal-shock resistance. |
| Zirconium Carbide | 3540 | Cermet component, refractory material, high-temperature electrical conductor. |
| Zirconium Oxide (Hafnia-Free Lime Stabilized) | 2593 | Thermal-barrier coatings for nuclear applications. |
| Zirconium Oxide | 2563 | Resistant to high-temperature oxidation to 2260°C, resists reaction to molten metals and pickup of product on annealing-furnace rolls and used on forging dies. |
| Zirconium Silicate | 1650 | Thermal barrier coating with good resistance to wetting by molten metals up to 1093 °C. |

Table 5: Results of chemical analysis

| substance | analysis (weight per cent) | | | |
|---|---|---|---|---|
| | Mo | C | Fe | O |
| $Mo/Mo_2C$ (50/50) (powder) | balance | 2,83 | 0,1 | 0,111 |
| $Mo/Mo_2C$-coating (sprayed in low pressure atmosphere) | balance | 2,6 | 0,15 | 0,12 |
| $Mo/Mo_2C$-coating (sprayed under atmospheric conditions) | balance | 0,8 | 0,1 | >1 |

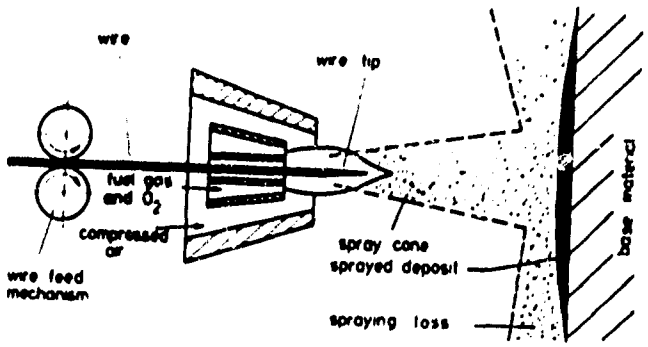
Table 6: Detonation-gun coating characteristics [13]

| Coating Composition | (% weight) | 99 %$Al_2O_3$ | 60%$Al_2O_3$ 40%$TiO_2$ | 80%$Cr_2C_3$ 20%NiCr (by volume) | 91%WC 9%Co | 87%WC 13%Co | 85%WC 15%Co | 25%WC 5%Ni Bal.mixed W-Cr carbides |
|---|---|---|---|---|---|---|---|---|
| Cross-sectional hardness, Vickers | (VPN 300) | 110 | 950 | 700 | 1300 | 1150 | 1050 | 1075 |
| Strength of bond to base metal | (lbf/in$^2$) | 10.000 | 9.000 | 18.000 | 25.000 | 25.000 | 25.000 | 20.000 |
| | N/mm$^2$ | 70 | 63 | 127 | 176 | 176 | 176 | 141 |
| Porosity | (%) | 1/2-1 | 1/2-1 | 1/4-1 | 1/4-1/2 | 1/4-1/2 | 1/4-1/2 | 1/2-1 |
| Density | g/cm$^3$ | 3.45 | - | 6,5 | 14,2 | 13,2 | 13,2 | 10,1 |
| Modulus of rupture | (lbf/in$^2$) | 20.000 | 19.000 | 70.000 | 80.000 | 90.000 | 100.000 | 40.000 |
| | N/mm$^2$ | 140 | 133 | 490 | 560 | 630 | 700 | 280 |
| Modulus of elasticity | ($10^6$ lbf/in$^2$) | 12.16 | 11 | 18 | 31 | 31 | 31 | 8 |
| | ($10^5$ N/mm$^2$) | 0.85 | 0.77 | 1.27 | 2.18 | 2.18 | 2.18 | 0.56 |
| Coefficient of thermal expansion | ($10^{-6}$/°F) | 3.8 (Avg. 70-1800°F) | - - | 6.4 (Avg. 70-1800°F) | 4.5 (Avg. 70-1000°F) | 4.5 (Avg. 70-1000°F) | 4.5 (Avg. 70-1000°F) | 4.6 (Avg. 70-1000°F) |
| | ($10^{-6}$/°C) | 6.8 (Avg. 20-980°C) | - - | 11.5 (Avg. 20-980°C) | 8.1 (Avg. 20-540°C) | 8.1 (Avg. 20-540°C) | 8.4 (Avg. 20-540°C) | 8.3 (Avg. 20-700°C) |
| +)Maximum operating temperature in an oxidising atmosphere | (°F) | 1800 | 1300 | 1800 | 1000 | 1000 | 1000 | 1400 |
| | (°C) | 980 | 705 | 980 | 540 | 540 | 540 | 760 |
| Main features | | Excellent resistance to wear, chemical attack and high temperature deterioration | Good wear resistance and self-mating properties. Semiconductor, excellent textile material | Good wear resistance at high temperature or in corrosive media | Extreme wear resistance | Excellent wear resistance and increased resistance to mechanical and thermal shock | Excellent wear resistance and greatest resistance to mechanical and thermal shock | Excellent wear resistance at higher temperatures. Improved corrosion resistance |

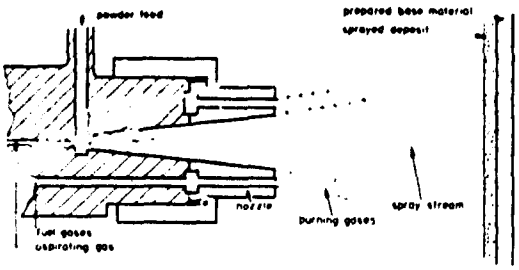
+) For short durations, considerably higher temperatures can be tolerated in many atmospheres; for example, for several minutes the 91%WC/9%Co-coating will resist flame impingement at temperatures up to 2200°C.

All data shown are average values derived from an extensive number of laboratory tests. It is well known that geometry and configuration of the plated surface will cause variations in many of the above characteristics and therefore they should not be taken as firm design specifications. Their purpose is for relative comparisons with other materials, and as guides for the design engineer.

Figures:




a) the wire form




b) the powder form [1]

Fig. 1: Principle of the flame-spraying process

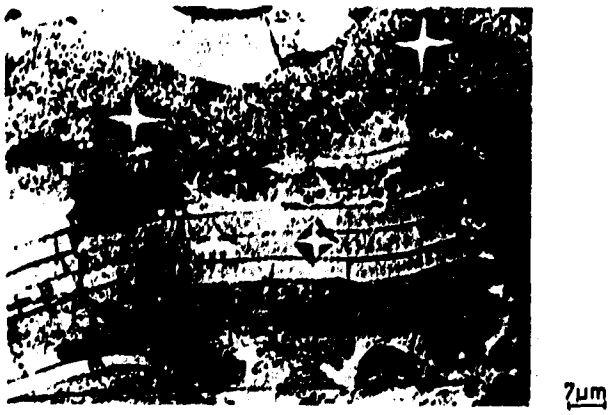



Fig. 2: Microstructure of a molybdenum coating, etching: Murakami

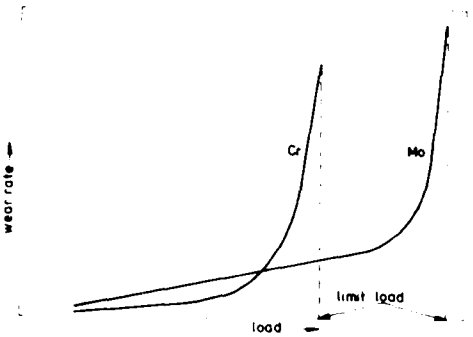



Fig. 3: Wear of hard chrome plated and flame sprayed molybdenum coating [4]

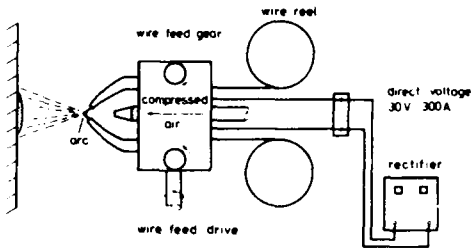



Fig. 4: Principle of the electric-arc spraying process

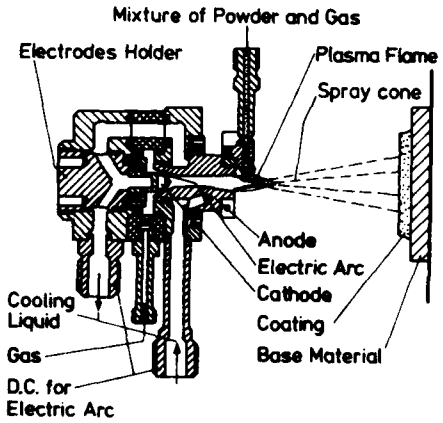



Fig. 5: Cross-section through plasma spray gun head

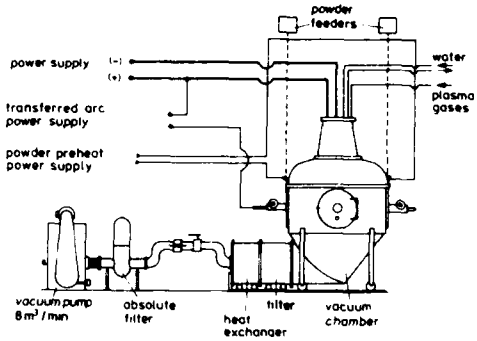
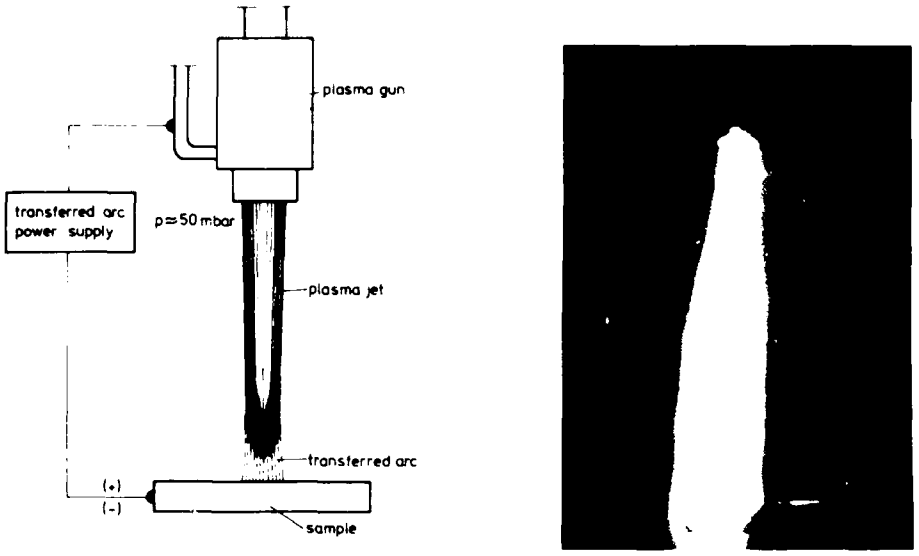



Fig. 6: System arrangement of the LPPS-facility

a) normal pressure b) low pressure (70 mbar)

Fig. 7: Formation of the plasma jet in different atmospheres




a) schematic drawing b) photograph

Fig. 8: Low pressure plasma spraying with additional transferred arc

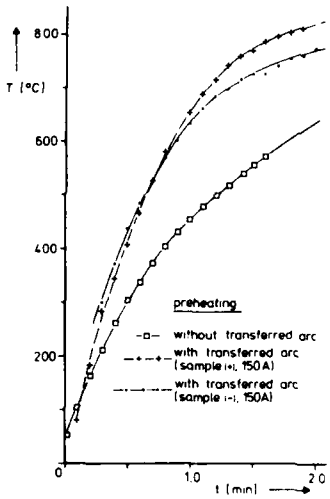
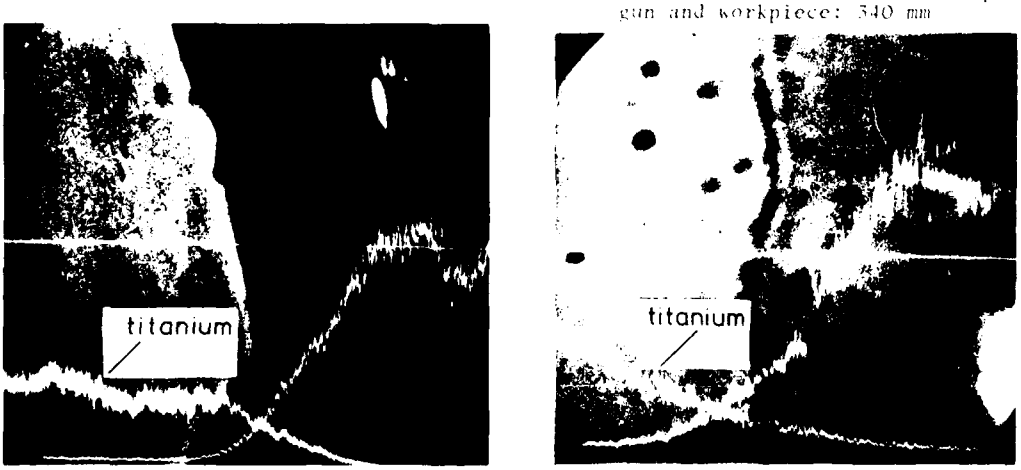



Fig. 9: Temperature gradient during preheating of a workpiece (100 x 100 x 10 mm³) with and without transferred arc. Distance between plasma gun and workpiece: 340 mm




a) without preheating b) with preheating by transferred arc (workpiece (-) poling) 5000 : 1

Fig. 10: Concentration gradient of iron and titanium, plasma sprayed on St 37 in a low-pressure atmosphere

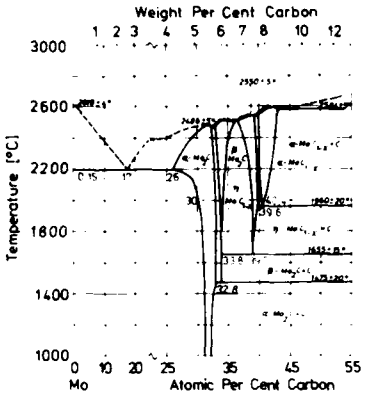
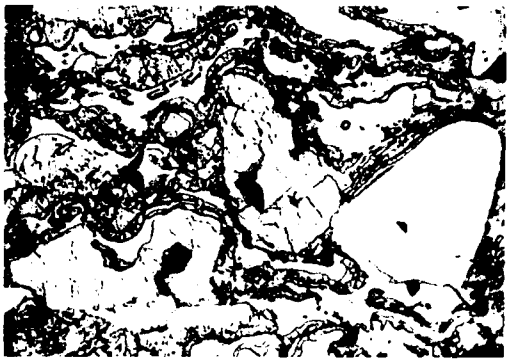



Fig. 11: Constitutional diagram C-Mo [12]



a) in a low-pressure atmosphere

b) in a normal atmosphere
1000 : 1
etching: Murakami

Fig. 12: Transverse micro-sections of Mo/$Mo_2C$-coatings

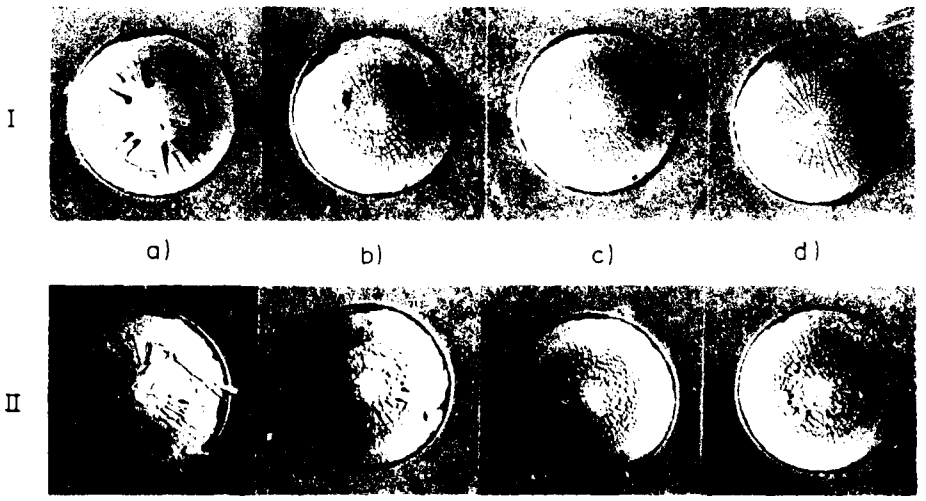



Fig. 13: Results of the indentation tests (Mo/$Mo_2C$ sprayed in a low-pressure atmosphere onto St 37)
Row I: Substrate subjected to grit blasting treatment before spraying
Row II: Substrate not subjected to grit blasting treatment before spraying
a) without transferred arc
b) transferred arc during preheating (workpiece positively poled)
c) transferred arc during preheating (workpiece negatively poled)
d) transferred arc during preheating (workpiece positively poled), during cleaning (negatively poled) and during spraying (workpiece positively poled).

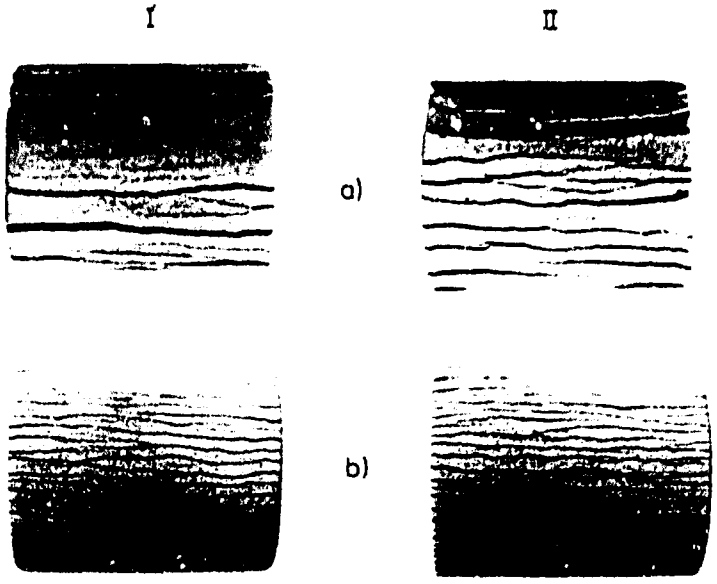



Fig. 14: Results of the bending tests ($Mo/Mo_2C$ in low-pressure atmosphere sprayed onto St 37)
Row I: Substrate subjected to grit blasting treatment before spraying
Row II: Substrate not subjected to grit blasting treatment
a) without transferred arc
b) see d, Fig. 13

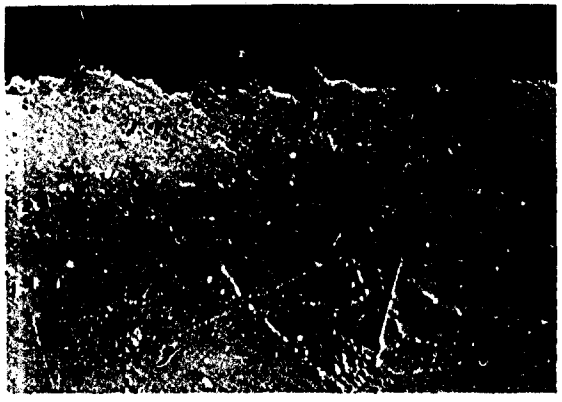


Fig. 15: Transverse micro-section of a CoCrAlY-coating sprayed in a low-pressure atmosphere (with transferred arc) 200 : 1, unetched

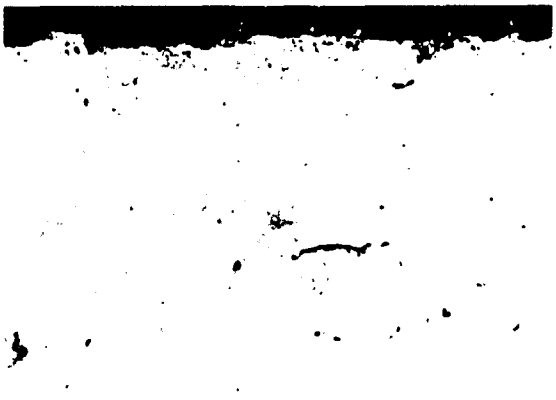


Fig. 16: Transverse micro-section of a copper-coating sprayed in a low-pressure atmosphere, 200 : 1, unetched

a) sprayed under atmospheric conditions b) sprayed in low-pressure atmosphere
Fig. 17: Transverse micro-sections of chromium-coatings unetched, 500 : 1

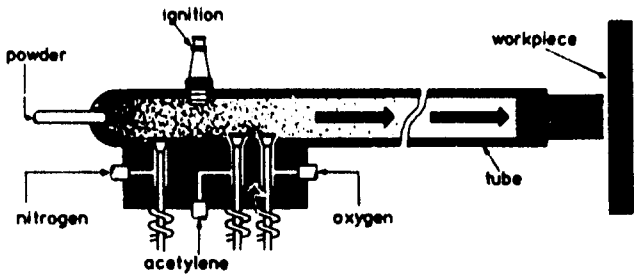



Fig. 18: Schematic representation of the detonation gun and its operation [13]

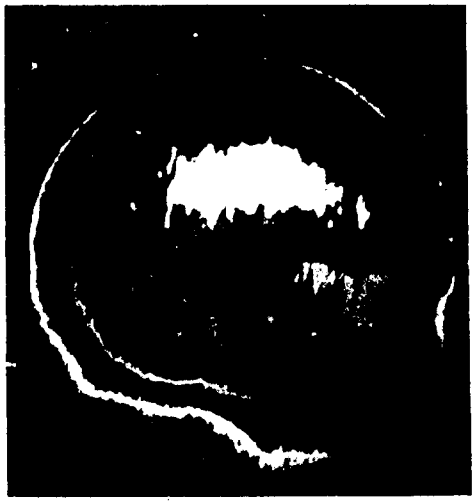


Fig. 19: Inhomogenous heat field at constant temperature

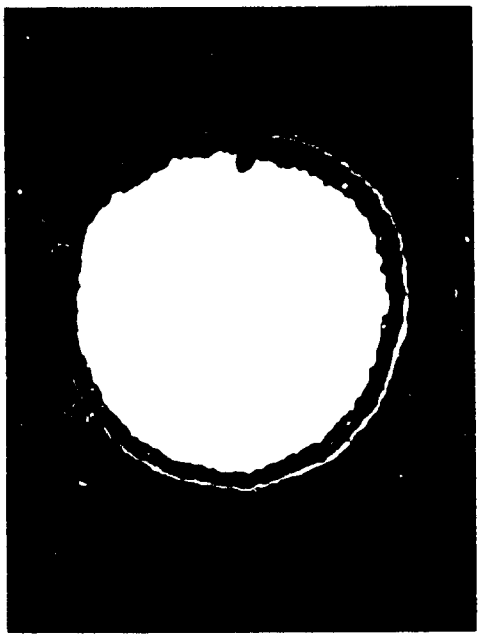


Fig. 20: Flaw detection during cooling down phase

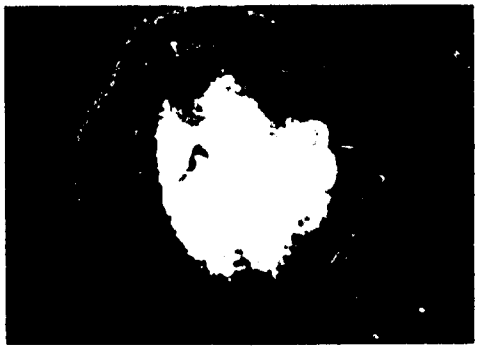


Fig. 21: Flaw detection during cooling down phase

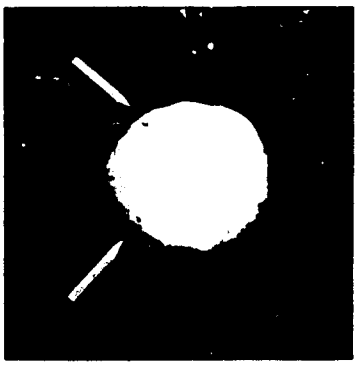


Fig. 22: Detection of smaller flaws

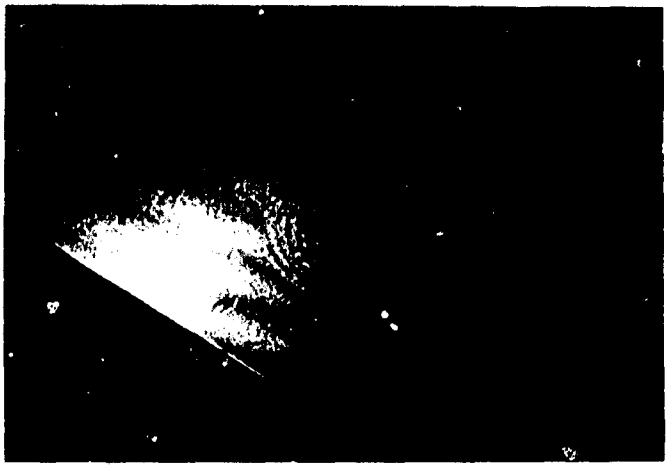


Fig. 23: Adhesion defect detected by optical holography

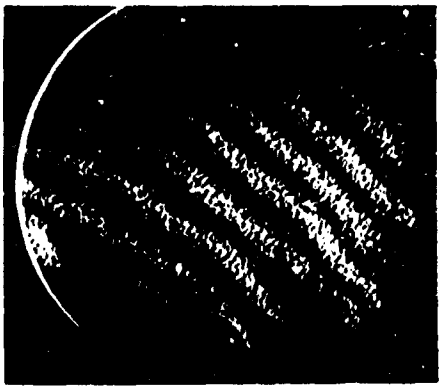


Fig. 24: Coating thickness irregularities detected by optical holography

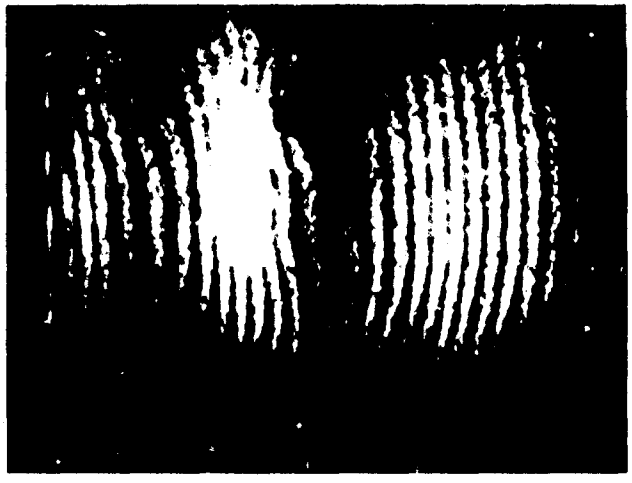


Fig. 25: Coating thickness irregularities: interferogram

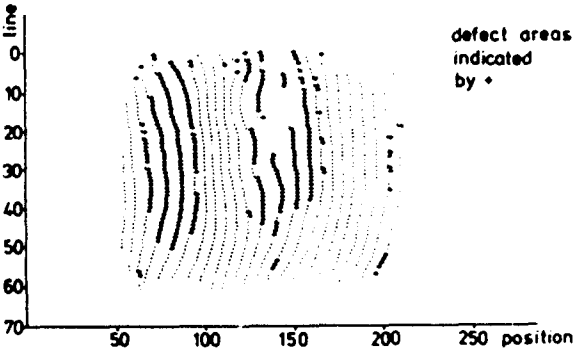



Fig. 26: Coating thickness irregularities indicated quantitatively by computer fringe evaluation program

Fig. 27: Ultrasonic wave, detected holographically on steel surface - no defect

Fig. 28: Ultrasonic wave, detected holographically on steel surface - wave distorted by a rechele

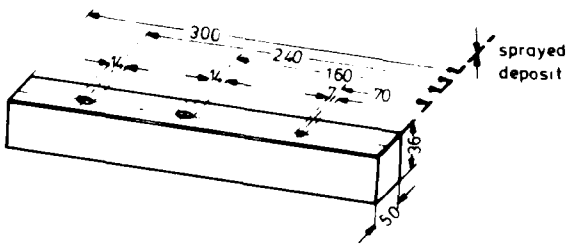



Fig. 29: Defect geometry

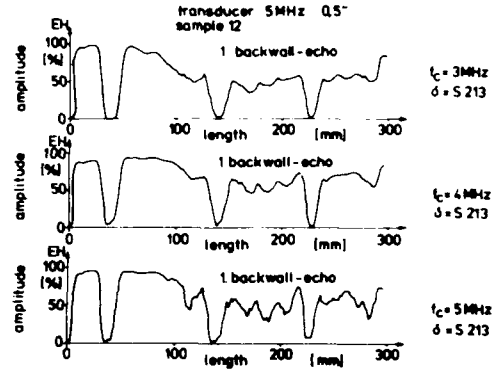



Fig. 30: Line scan using different frequencies, single transducer

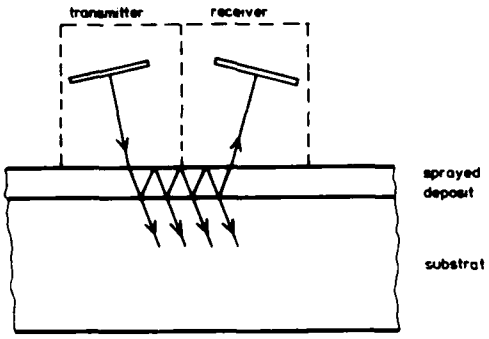



Fig. 31: Testing of sprayed deposits with a twin probe

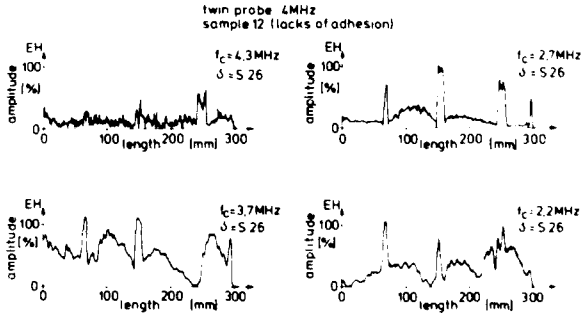



Fig. 32: Line scan using different frequencies, twin probe

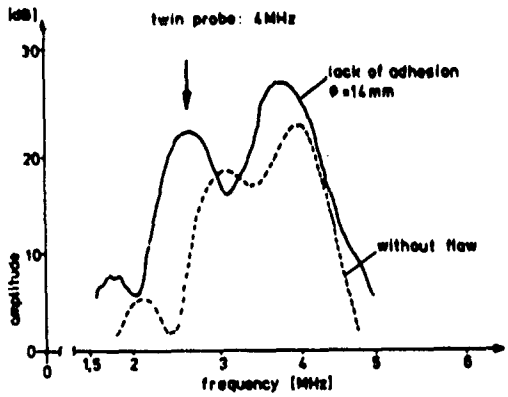



Fig. 33: Spectra of interface echoes

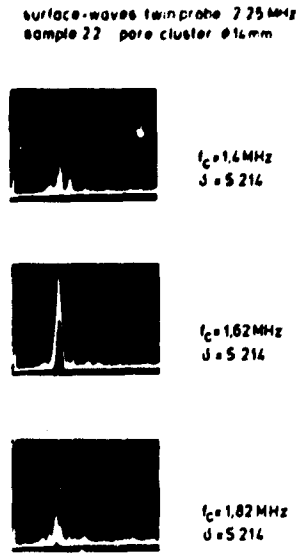



Fig. 34: Testing with surface waves at different frequencies

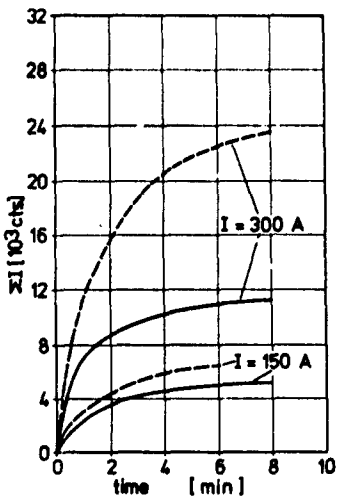



Fig. 35: Influence of current intensity on acoustic emission

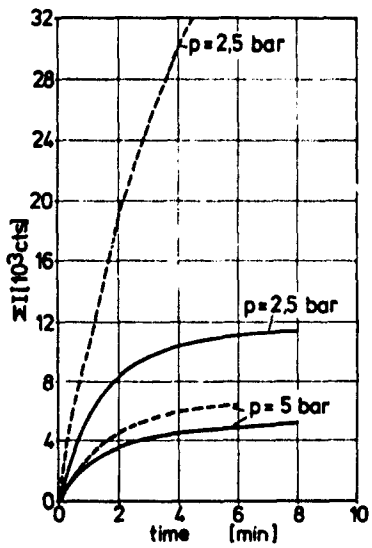



Fig. 36: Influence of air pressure on acoustic emission

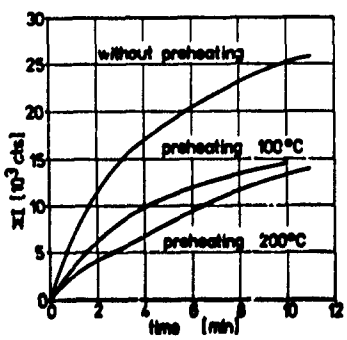



Fig. 37: Influence of substrate preheating on acoustic emission

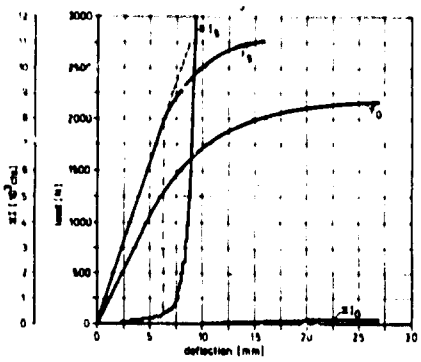



Fig. 38: Acoustic emission during bend test
index S: sample with sprayed coating
index G: sample substrate only

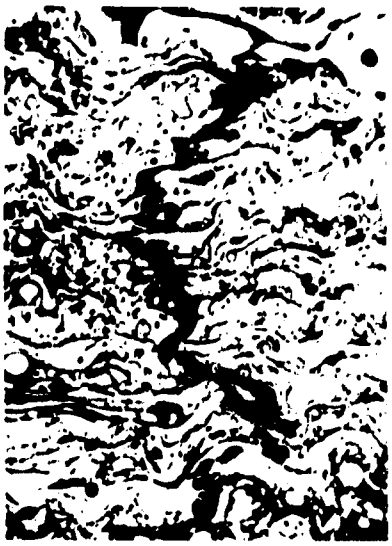


Fig. 39: Cracks in sprayed coating; load until fracture (F = 2750 N)

# LASER SURFACE ALLOYING

by: P.G. CAPPELLI
CENTRO RICERCHE FIAT SpA
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## INTRODUCTION

The process utilized to modify the surface characteristics of a material can be of various nature depending on the chemical and physical properties of the material itself as well as on the type of modification to be achieved. A first group includes those processes which result in a so called overlay coating, that is where an alloy or a compound is deposited on a base material with minimal interaction or interdiffusion phenomena taking place (e.g. Cr plating). A second category includes those process which imply the modification of the chemical composition of the microstructure of the surface of a material in order to improve some of its properties.
Within the second category, a number of new techniques based on high power lasers now have emerged, offering potential solutions to both the high melting point and segregation problems in the fabrication of metal and ceramic alloys. These lasers are already gaining acceptance in such materials processing areas as deep penetration autogenous welding, cutting, drilling, transformation hardening and experimental shock hardening.
The very high power densities that lasers can produce, equivalent to thermal sources of temperatures above 20000°C, facilitate the melting of all phases of the alloy. Furthermore, the high power density of lasers also allows melting to be localized at the surface, with negligible sub-surface heating, thereby establishing high cooling rates. In this process, called "laser glazing" the extremely rapid chill rates of thin molten zones have produced a variety of novel, extremely homogeneous metallurgical microstructures, including amorphous alloys, the ultimate in alloy homogeneity.

## LASER SYSTEMS

The concept of a pencil-like laser beam which can be transmitted to great distances with very little attenuation is now a familiar notion. Such beams are now commonly used in surveying instruments and alignment tools for assembling large mechanical structures. In general, this type of laser operates at a power level of about one milliwatt, with a wavelength in the visible. Higher power lasers, in the 1 to 300 watt range, which operate in both the visible and the infrared, have beem gaining more and more acceptance in the micro machining, welding and cutting of sheet metal and plastic.
In contrast with this situation recent advances in laser technology have resulted in the production of $CO_2$ lasers with a power level in the 1000 to 20000 watt range and electrical efficiencies of 10-15%. These lasers utilize carbon dioxide ($CO_2$) as the active gas, and radiate at a wavelength in the far infrared (10.6 micron), well beyond the visible spectrum. However the ability to transmit the beam over large distances with relatively little attenuation, and to focus the beam to a very small spot is similar to those capabilities for the low power lasers.
With such lasers metals have been, cut and welded (ut to 50 mm thicknesses), surface hardened and alloyed (1.5 mm case depth).

### Categories of Multi-kilowatt Lasers

It is helpful in understanding the state of the art of multi-kilowatt lasers to categorize gas laser into three categories (See Fig. 1).

#### Class 1

In the ordinary discharge tube laser the gas is cooled by heat conduction to cooled side walls. Since $CO_2$ lasers cannot operate efficiently at temperatures much above 200°C, the maximum electrical power which can be delivered to the glass tube must be less than about 525 watt/m of discharge tube. At a 15% conversion efficiency, this corresponds to an output power of 79 watt/m. At higher input powers, the gas could overheat and the output power would not increase. Even if the tube diameter were increased beyond the 25 to 50 mm range commonly used, the input power still could not be increased above 393 watt/m because the gas in the center of the tube would overheat due to the longer conduction path to the cooled wall.
If the gas pressure were increased to provide greater heat capacity, the uniform electrical flow discharge between electrodes (characteristics of low pressure discharges) would become filamentary in nature and significantly reduce the laser output.
Thus the only way to increase the output power from a Class 1 device is to increase the length of class tube Laboratory devices of this category have been operated with near diffraction limited outputs at powers approaching 10 kilowatt, but the length of there devices is of the order of 120 m of glass tubing.
Tipically the basic structure is a large, vertically mounted granite block to which are attached the glass discharge tubes.
Six of these tubes (3 per side) approximately 2 m long, are arranged in a "Z" pattern, with mirrors at each intersection to reflect the beam from one tube to the next.

#### Class 2

By utilizing a rapid flow of gas through the discharge tube, the waste heat can be removed by convection rather than by conduction. Since convective heat removal is greater than conduction, greater input power den-

[illegible] be utilized without any increase in gas and temperature. This axial flow type of device is referred to as a Class 2 device (See Fig. 1). A variety of Class 2 devices has been successfully operated in a closed configuration, with near diffraction limited output beams at power levels up to approximately 6 Kwatts. In these devices the discharge still takes place in a series of long glass tubes, with the discharge direction parallel with the flow direction. The tube diameter is sufficiently small and the pressure is sufficiently low so that, as in the Class 1 devices, diffusion of the electrons to the walls is the mechanism to produce the uniform electric discharge. The specific output power capabilities of this class of laser is approximately 650 W/m.

Class 3

In the Class 3 devices, the gas flow is perpendicular to both the electrical discharge and optical axis giving rise to a cross flow configuration, in contrast to the axial flow configuration of the Class 2 devices. The principal advantage of this configuration is that the lasing gas dwell time in the optical cavity is much shorter than with the axial flow deviced, resulting in the possibility of much higher power densities and consequently much more power per unit length of optical cavity. However, since there are no glass walls to stabilize the electric discharge, as there were in both the Class 1 and Class 2 devices, some other form of discharge stabilization must be used. Generally, but not always, it is necessary to ionize the lasing gas, and make it electrically conducting. The main, or sustainer electric power, is then delivered to this conducting region of gas, and the resulting discharge is uniform, and free of filaments.
In one configuration, the gas ionization is accomplished through the use of a large area, low power electron beam which irradiates the optical cavity. The E-beam is fired perpendicular to both the gas flow and the optical axis. The sustainer discharge is in the same direction as the E-beam, and the axis of the optical cavity is perpendicular to both the flow direction and the discharge direction. This process is used in the Avco 15 KW laser shown in Figure 2.

NEW LASER TECHNIQUES

The ability of continuous, high power laser to generate power densities of up to $10^8$ watt/cm$^2$ makes them useful for a variety of materials processing techniques. Fig. 3 displays the spectrum of laser materials interaction located on a plot of laser power density and interaction time. The materials processing effects now being utilized include:

- deep penetration laser welding
- laser cutting
- drilling of holes
- heat treating by transformation hardening
- surface alloying.

Although the number of industrial manufacturing jobs that are currently being done by each of these laser operations varies from a few (welding, surface alloying) to a large number (cutting), it must be remembered that laser materials processing is still a young and growing technology.
Two further techniques for materials processing by laser have been proposed more recently, and these are already well into the research and development stage.

- Laser shock hardening attempts to work harden materials with the blast wave that accompanies rapid surface vaporization induced by pulsed lasers at very high power densities, over $10^9$ W/cm$^2$.

- Laser glazing, a new and elegant method for reproducibly and controllably attaining rapid solidification and solid-state cooling of materials. The technique of laser glazing involves rapidly traversing the surface of a material with a laser beam focussed to a power density in the range of $10^4$ - $10^7$ W/cm$^2$.
  This procedure yelds a thin melt layer at close to 100% melting efficiency; that is, the substrate remains cold. Due to the steep temperature gradient established by the process, rapid solidification and subsequent solid state cooling take place following the passage of the laser beam. Average quench rates in excess of $10^8$ °C/sec have been achieved in melt thicknesses in the 1-10 micron range, with correspondingly lower quench rates in thicker sections.
  Some valuable features for materials research by the laser-glazing technique are that it is relatively inexpensive, highly controllable and reproducible. The process is already being used to screen large numbers of candidate alloys for programs aimed at developing new alloys with beneficial structures. If any of these alloys are to be used in the amorphous (glassy) state, their applications will be limited to those at relatively low temperatures, below the instantaneous glass transition temperature.

SURFACE ALLOYING

If the beam power is sufficiently high and the material can absorb the incident radiation, local melting is, as said, possible: the power density required is approximately three times that for transformation hardening in the solid state.
By rapidly scanning the beam, local melting of large areas can be produced. The effect is equivalent to creating a thin molten skin at the surface. One obvious way to take advantage of this possibility is to eliminate surface defects and to produce hard surfaces in cast irons either by martensitic transformation or by carbide formation.
Much greater potential exists, however, for the production of surface regions of markedly different chemical composition from the bulk material, by adding alloying elements to the liquid metal zone. This is known as surface alloying and enables a part to be made of a cheap base material and then, by modifying the surface

chemistry, produce corrosion and wear resistant characteristics on the surface of the component. An example of use is on valves and valve seats which are commonly treated with hardfacing alloys such as stellites. Laser surface alloying provides for more economic use of the expensive alloying elements e.g. Cr, Co, W, etc, cuts down on machining operations, and increases productivity by reducing processing time per component. With this technique, a part can be fabricated from a base metal selected on the basis of cost and mechanical properties, and the working surface can be modified to provide the characteristics required by the application. Since many metal elements can be alloyed into the base metal, at alloy concentrations in excess of 50% if needed, freedom in part design can result in substantial product improvements and cost reductions. For example, if a part is subject to impulsively delivered mechanical loads, it must be made of a very tough, crack-resistant material such as AISI 4815 steel.
However, if that same part has a bearing that must be very hard to resist wear, particularly at elevated temperatures, the surface chemistry must be modified.
This has been accomplished by adding carbon and chromium to the alloyed region. Since the region cools very rapidly, the resulting dendritic structure is quite fine, and contains chromium carbide in the interdendritic regions. This type of structure retains its hardness quite well, even at elevated temperatures, due to the relatively high chromium content in the alloyed region(Fig. 4. In this case, surface chemistry modification by laser alloying can be applied on line at high production rates, rather than employing a long off-line processing technique, such as carburizing.
Prior of looking into other specific examples of laser alloying application, another aspect to be considered is the possibility of prediction and controlling the actual structure of the alloyed region, as well as the process parameters to be employed. This has been done in the case, already mentioned, of chromium alloying of a carbon steel.
The mathematic model utilized is a well known and simple one, developed to describe heat propagation into a material, in accordance with the heat conduction equation

$$\frac{\partial^2 \varphi}{\partial x^2} - \frac{I}{R}\frac{\partial \varphi}{\partial t} = \dot{\varepsilon}\ Fo$$

and with the boundary conditions for the radiation of an infinite surface (Carslaw and Jaeger).
This model can describe heat propagation into a body made of two layers of different materials, provided the two following boundary conditions are satisfied:

- ideal thermal contact between the surface of the two materials
- uniform energy flow into the radiation surface

From the model the parametric curves have been obtained correlating power density with alloyed depth for various radiating times (Fig. 5). To be applicable to practical case, the model must assume that the thickness of the base material is much greater than the depth of the alloyed region (Fig. 6).
Furthermore, the heat input from the laser beam must be such to induce state transformations in a negligible time.
Fig. 7 shows the results obtained in the case of chromium alloying of a carbon steel.
The experimental results fit satisfactorily with the model, the spreading becoming greater as the experimental conditions approach their limit value (dotted line).

## SURFACE ALLOYING OF ALUMINIUM

Aluminium alloys find a wide range of applications in engine components mainly because of their low specific weight and ease of processing (casting).
On the other side their use is limited by their scarce thermal resistance and surface hardness. These properties can be substantially improved through the creation of surface layers which specifically respond to the above requirements.

### Ni-Cr Alloying

The better resistance of Ni-Cr alloys to low cycle (thermal) fatigue suggests Ni-Cr alloying localized to regions where aluminum alloys are subject to thermal stresses in the engine head. To establish the feasibility of such application, aluminum samples have been alloyed with Ni and Cr.
The samples, 70 x 70 x 10 mm, had a groove to contain the alloying powder and to avoid excessive spreading during the treatment. Furthermore, as the heat transfer between the powder and the base metal, is poor, the samples have been sand blasted to increase the surface absorption coefficient and to avoid rapid melting of the powder without melting of the aluminum. The power level employed was in the range 10-14 KW and the process was carried out at a speed of 200 mm/min. In both cases the treatment resulted in a uniform metallurgically bonded alloyed layer (Fig. 8).

### Si Alloying

Aluminum engine blocks usually require cast iron cylinder liners, while aluminum alloys with a silicon content well in excess of the eutectic could give surface hardness sufficient to avoid the linears. Laser surface alloying with silicon has the problem associated with the low density of Si and its low heat of evaporation. The silicon powder must then be applyed in a different way.
Si powders were plasma sprayed on the Al samples and subsequently laser treated at a power level of 6 KW and a travel speed of 200 mm/min. Silicon concentration as high as 50% were obtained with a microstructure much finer than in normal hypereutectic alloys (Fig. 9).

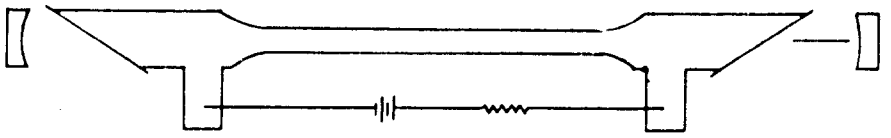
SURFACE ALLOYING OF STEEL

Many applications where corrosion resistance is needed require the use of stainless steels or even super-alloys in massive even if the bulk properties of a normal carbon steel could be sufficient.
This fact bring to a not necessary use of strategic elements such as Ni and Cr.
Medium-carbon steel samples have surface alloyed with Ni Cr Al to create a layer with improved corrosion resistance.
Also in this case the samples were sand blasted and a groove machined to improve radiation absorption and avoid excessive spreading of the alloying powders.
The laser power level was in the range 13-14 KW and the travel speed 200 mm/min. The resulting layer showed a uniform structure and composition as indicated in Fig. 10.

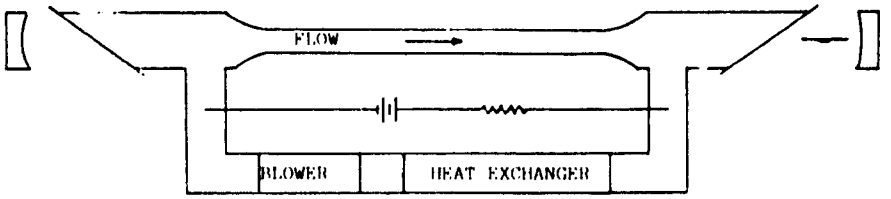
SURFACE ALLOYING WITH CARBIDES

Wear and erosion resistance of various materials can be improved through the formation of a carbide rich surface layer. This is rather easily possible with laser surface alloying either using the normal practice of powders melting or, starting with the metal powders and graphite, promoting the in-situ formation of the carbide.
Figures 11, 12 and 13 show three examples of carbide alloying, VC and WC on carbon steel and TiC on titanium, whereby the WC has been obtained employing a mixture of tungsten and graphite. The use of graphite powder has the advantage of assuring a good absorption coefficient of the laser beam.
The process parameters employed were power level in the range 9-14 KW and travel speed between 100 and 250 mm/min.

CLASS 1 DEVICE: HEAT REMOVAL AND DISCHARGE STABILIZATION BY DIFFUSION TO CAVITY WALLS.



CLASS 2 DEVICE: HEAT REMOVAL BY RAPID FLOW, DISCHARGE STABILIZATION BY DIFFUSION TO CAVITY WALLS.




CLASS 3 DEVICE: HEAT REMOVAL BY FLOW, DISCHARGE STABILIZATION BY PRE-IONIZATION. PRACTICAL POWER GREATER THAN 10 kW.

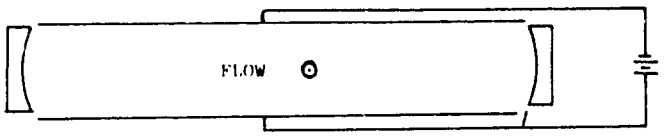



Fig.1 Classes of electric gas laser devices

**Fig.2 Class 3 AVCO 15 kw high power laser**

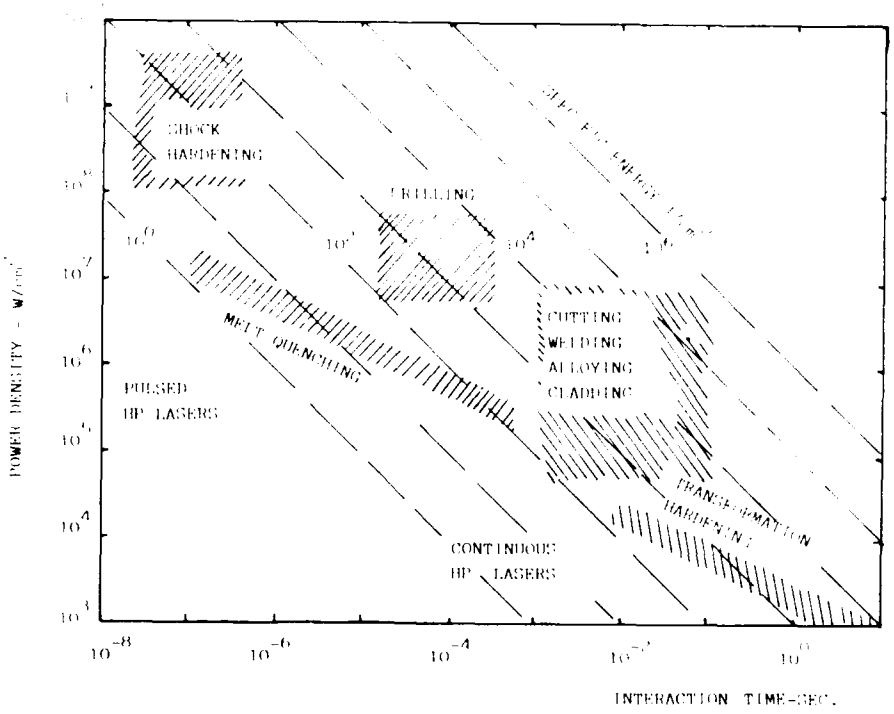



Fig.3 Operational fields for laser processing in metals

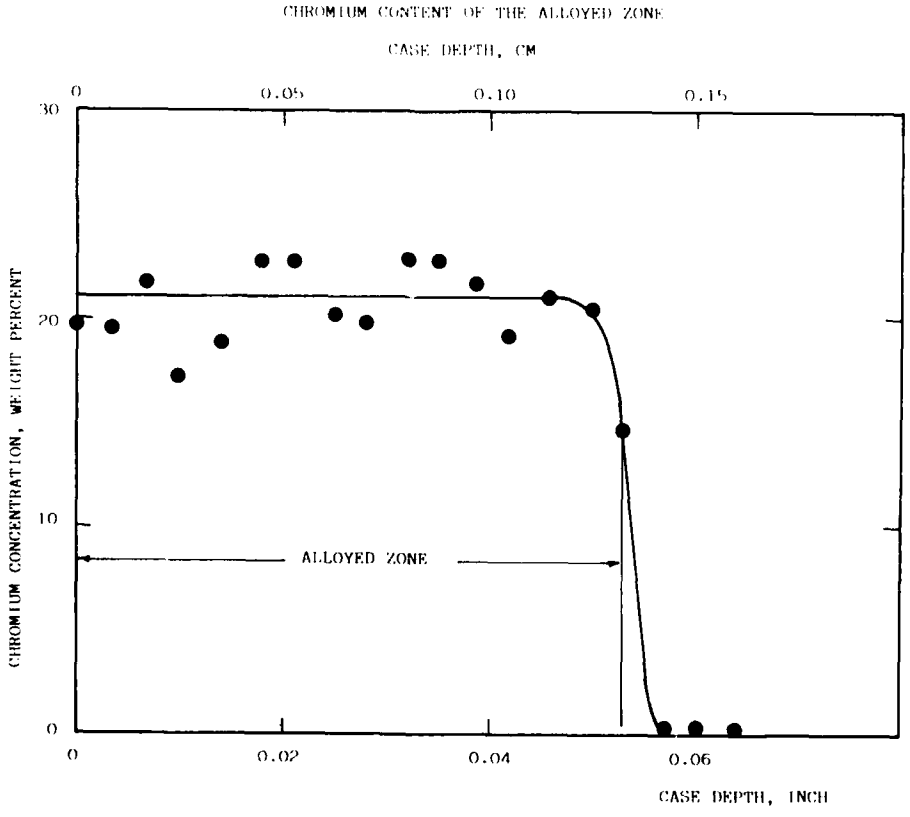



Fig.4 Chromium concentration in laser alloyed AISI 4815 steel

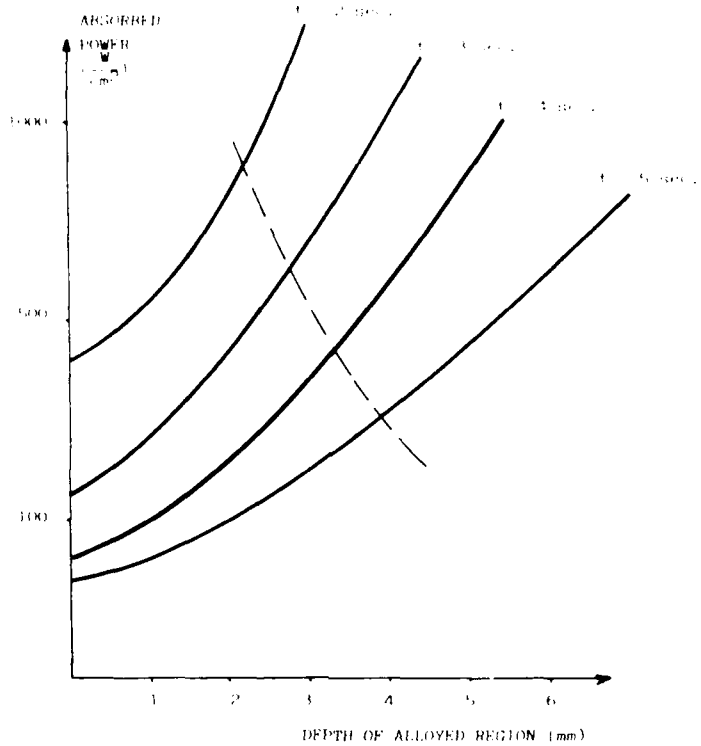



Fig.5 Correlation between power density and alloyed depth for various radiating times

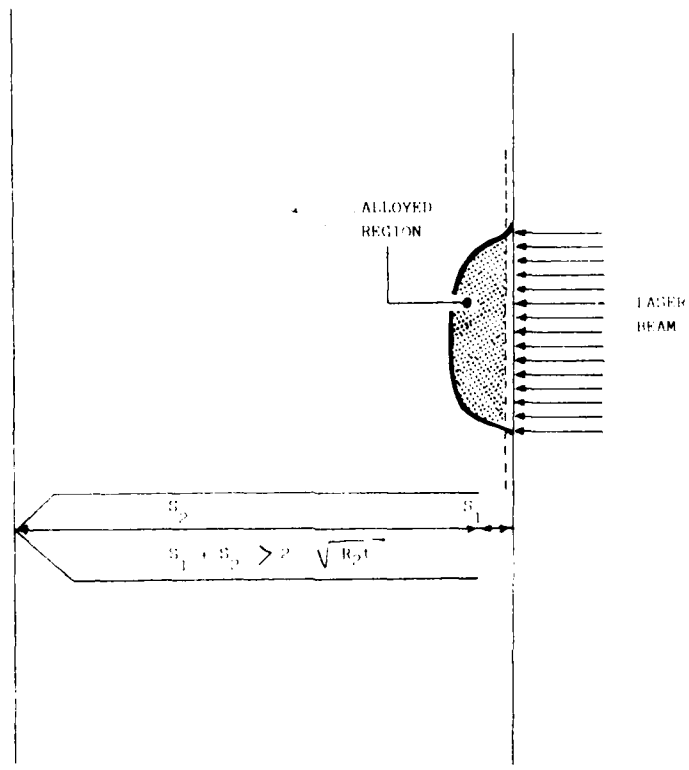



Fig.6 Schematic representation of assumption made for validity of model

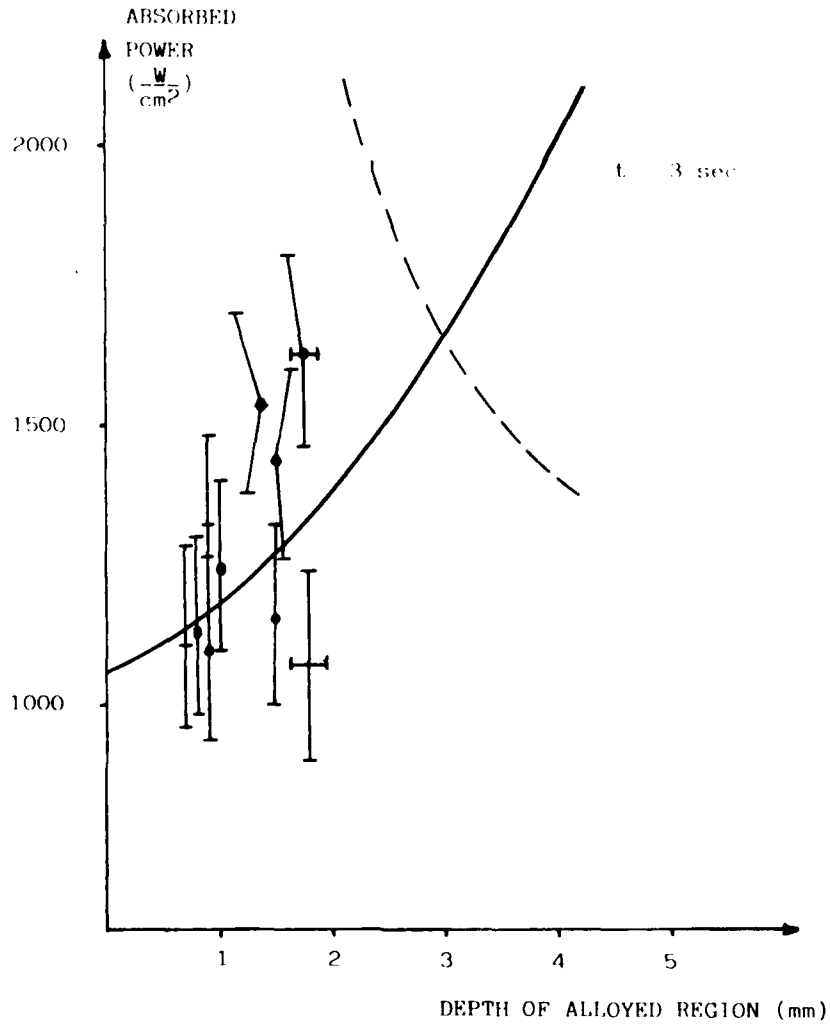
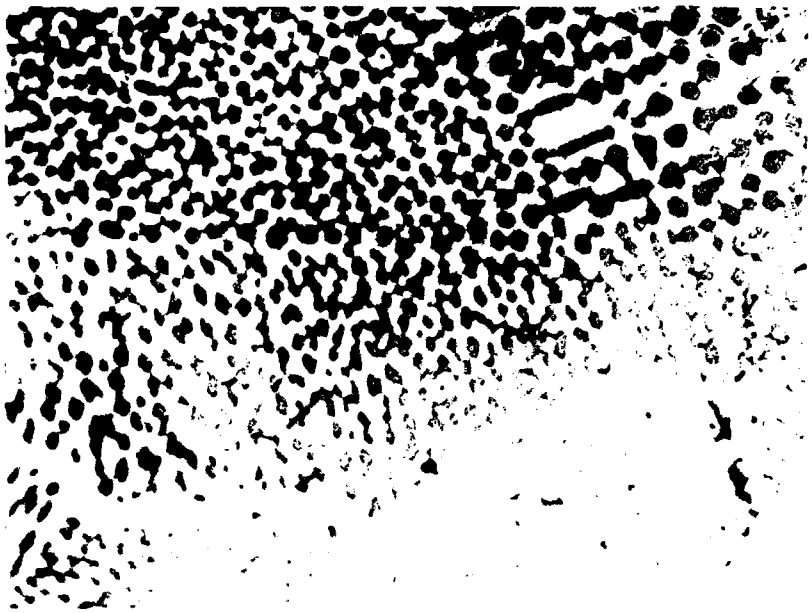
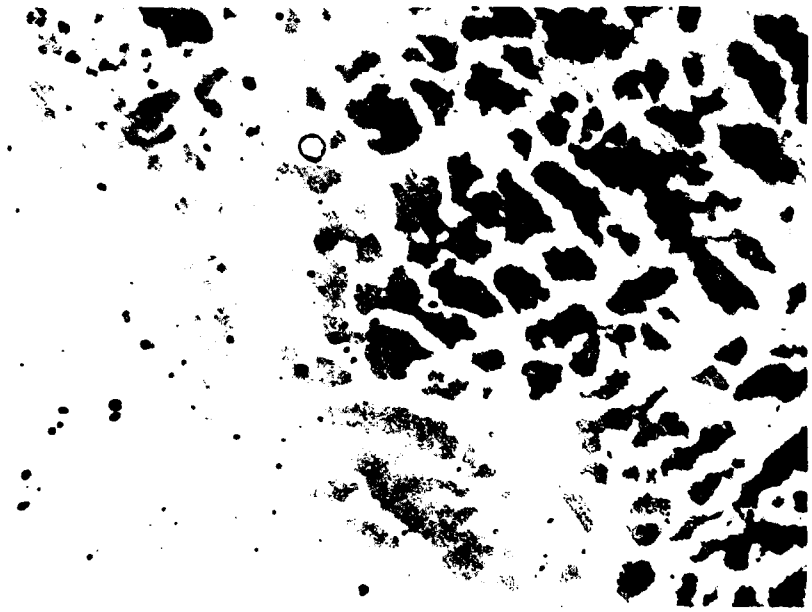



Fig.7 Correlation between experimental results and model



(a) Ni alloying of Al (x 300)



(b) Cr alloying of Al (x 120)

Fig.8 Surface alloying of Al

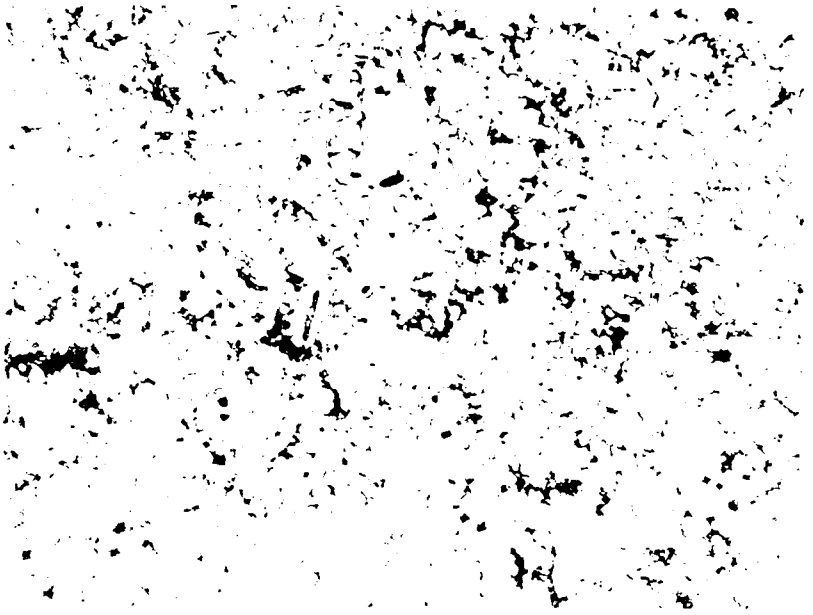
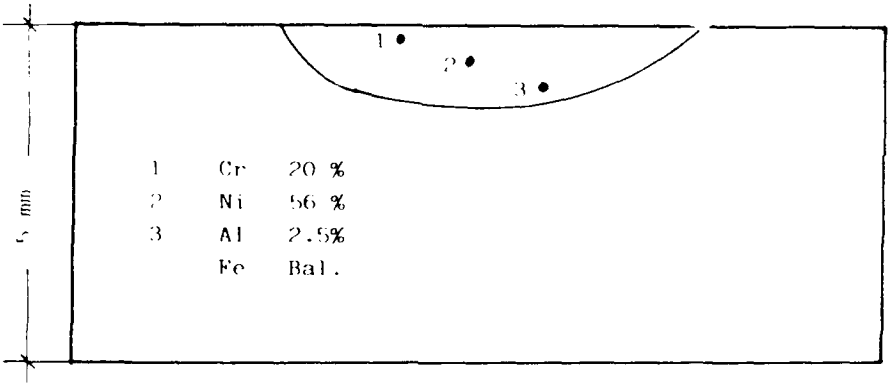


Fig.9 Silicon alloying of Al. (Si concentration above 50 % (X 500)




x 300

Fig.10 Ni Cr Al alloying of carbon steel

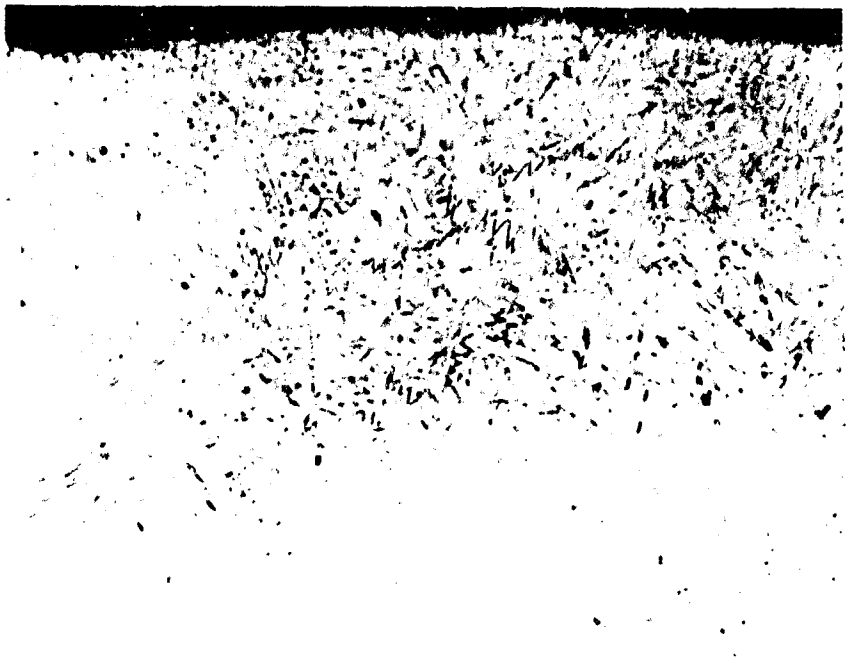


Fig.11 Vanadium carbide alloying of carbon steel (x 500)

Fig.12 Tungsten carbide (tungsten plus graphite) alloying of carbon steel (x 500)

Fig.13 Titanium carbide surface alloying of titanium alloy

# CORROSION PROTECTION BY ELECTRO-DEPOSITED ALUMINIUM

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SUMMARY

Aluminium can be deposited on various substrates by using a nonaqueous organic electrolytic system. The metallic deposit has a very high purity and good corrosion-protection properties. It can be used as a substitute for the highly toxic cadium, which is dangerous to the environment.

Possible fields of application are protection against corrosion of high-strength steels without any danger of hydrogen embrittlement, the coating of lightweight materials like aluminium, magnesium and titanium alloys and the fabrication of fibre-reinforced metal matrix composites.

MBB have installed a facility for the electro-deposition of aluminium and have worked in this field for more than three years. This paper discusses the experience and experimental results of the new technology and the possible advantages compared with other techniques.

## 1. The Electro-deposition of aluminium

### 1.1 Electrolyte systems

Because of the strongly negative electrochemical behaviour ($E_0/H_2$ - 1.67 V : 25°C) aluminium cannot be desposited out of aqueous solutions. In an electrolytic cell, containing an aluminium salt solution, only hydrogen would be developed on the cathode by the application of an electric field.

A lot of work has been done to develop electrolyte systems for aluminium deposition using melting salts or nonaqueous organic solutions (1, Tab. 1). Only a few of these processes have reached considerable technical importance and can be applied in an industrial stage. A nonaqueous electrolyte consisting of aluminium chloride and lithium hydride in an etherical solution has been developed by S.H. Couch and A. Brenner (2,5) and has been used by NASA and contractors (General Electric, Electro Optical Systems Inc. et.al.) for various applications (3,4), e.g.

- Space hardware (solar cells, solar concentrators, corner mirrors, aluminium-lined pressure vessels, lenses for telescopes, cameras)
- Nuclear applications(aluminium-cladded reactor fuel elements)
- Aircraft industry (aircraft wings, high-pressure tanks, coating of high-strength steel and titanium fasteners, composite materials)
- Electronic industry (nonmagnetic composites, ligthweight wave guides, corrosion-resistant coatings).

The electrolyte systems used have some serious disadvantages which seem to be an obstacle to the application on a large industrial scale.

- The combustibility of lithium aluminium hydride containing etheral solutions is very high; the compound containing aluminium is very sensitive to oxygen, moisture and carbon dioxide and tends to immediate inflammation in contact with these materials.
- Since aluminium chloride produces hydrochloric acid in contact with water, there will be a constant danger of corrosion on coated parts or installations.
- Lithium aluminium hydride forms hydrogen by decomposition. This hydrogen can penetrate into metallic lattices and cause hydrogen embrittlement, e.g. in high-strength steels.

Electroplating from fused-salt baths is a second way for the electro-deposition of aluminium. This technology, too, has serious disadvantages.

- Because of the high operating temperature (700 to 1000°C) there is the danger of degradation of the mechanical properties of the basic materials (recrystallisation, diffusion of alloy components, embrittlement) and of distortion of complicated parts.
- The electrolytes are built up from compounds containing halogens.They are extremely corrosive and form a danger to materials and installations.
- Because of the necessity to deposit at high current densities, the electrical equipment for a fused-salt bath is very expensive.

1.2 Complex organic solutions
(Siemens-Process)

An electrolyte consisting of a complex mixture of aluminiumalkyl and sodium fluoride in toluene has the following advantages as compared with the previously described systems (1,6,7,8):

- no danger of thermal degradation of the basic materials (process temperature below 100°C)
- no hydrogen in the ionic state is present within the electrolyte or can be produced by degradation: therefore, any danger of hydrogen embrittlement of sensitive materials (e.g. high-strength steels) does not exist
- the electrolyte contains no halide compounds wherefrom results that there is no danger of any formation of aggressive components and that no parts and installations will be subject to corrosion
- because of the highly selective electrolyte system (only aluminium and a very limited number of elements can form alkyls) very pure aluminium is deposited; absence of secondary reactions additionally causes a very high cathodic current efficiency
- due to the application of special precautions (working under inertgas, preventing the penetration of oxygen and moisture into the electrolyte), the useful life of the electrolyte is very long. Contamination products of oxygen and water (formation of alkoxy compounds) are soluble in the electrolyte and produce no slurry. Trace elements from the anode material are not soluble in the electrolyte.

In addition to these important facts, the electrolyte system fulfils the conditions required for an electroplating bath like sufficient macro- and micro-throwing power, applicability on an industrial stage and economical processing (long life of electrolyte and equipment, inexpensive basic chemicals). It is an extremely important fact that complete recycling of all waste products is possible. Therefore, there is no danger of contamination of the environment. Unlike the toxic and environmentally dangerous cadmium, aluminium is a nontoxic material. For this reason, no contamination of the environment is possible by primary (waste products, waste waters) or secondary reaction products (corrosion in service).

The deposition of very pure aluminium is caused by the use of a highly selective electrolyte system. The chemical composition of the standard electrolyte and the average process parameters are summarized in Table 2.

Fig. 1 shows the electrochemical reactions and processes taking place on the cathode and anode of the electrolytic cell. The anode consists of aluminium, usually very pure material to avoid contamination of the electrolyte by particles of alloy elements. There is no danger of passivation of the anode by using less pure aluminium, but the formation of a non-soluble layer may cause reduced metal solubility. An increase of the inner resistance (which is already high in the organic system because of the limited number of ions per volume unit) of the electrolytic cell and the necessity to work with higher voltages will result, and bad deposits may be formed.

Due to the fact that only a very limited number of chemical elements can form alkyls (in particular aluminium, gallium, indium, thallium), only aluminium can be solved anodically by the attack of the alkyl radicals. The contaminants in the aluminium anode remain completely unsolved. This anodic reaction is the main reason for the high purity of the deposit ("if only aluminium is solved, only aluminium can be deposited"). The decomposition products of the electrolyte (in particular alkoxy compounds formed by contact with oxygen and humidity) are soluble within the electrolyte up to a very high percentage. The only danger of contamination is by inclusion of particles from the anodic slurry or from the pretreatment. To avoid incorporation of slurry particles, the anodes are usually coated with bags of an electrolyte-resistant material. The products of mechanical pretreatment operations must be removed by carefully rinsing with nonaqueous solutions under application of ultrasonics.

1.3 Properties of electro-plated aluminium

Owing to the highly selective electrolyte system very pure aluminium is deposited by the Siemens-Process. The following properties have been studied to be typical for electroplated aluminium (6,7)

- extremly pure metal (aluminium content not lower than 99,99%)
- micro-crystalline structure with a grain size of less than 1 µm
- dense and porefree deposit due to the non-orientated small grain size deposition
- good ductility and formability due to the extreme purity (lack of incorporations)
- good adhesion to various basic materials by the application of substrate pretreatment procedures
- good thermal and electrical conductivity
- nonmagnetic behaviour (important for various electronic applications)
- high resistance to various environmental conditions due to the formation of tight, good-adherent oxide layers
- good corrosion resistance to various aggressive chemicals
- protection against corrosion of nobler materials because of the function as a sacrificial anode (long-distance protection)

- good ultrasonic weldability
- anodizing and colouring is possible
- the metal can be deposited in thick layers (electroforming) for special applications.

1.4 Plating equipment

Since the organic electrolyte system is very sensitive to oxygen and humidity, various precautions must be taken to guarantee a sufficiently long life and economical processing. Based on the experience of Siemens with laboratory and smallscale test equipment, we have installed a 400 liter cell in our electroplating facility near Munich, Federal Republic of Germany. Fig. 2 shows the coating unit in the centre, flanked by degreasing and blasting equipment on both sides. Fig. 3 shows details of the cell, on the right side of the picture, we see a device for processing small parts.

The electro-plating cell consists of two compartments. The basic tank containing the electrolyte is closed by a large air-lock with doors at the top and on the bottom. This air-lock and the empty space over the surface of the electrolyte is flooded with purified nitrogen under a slight overpressure. The equipment for the movement of workpieces is located under the bottom door, which is permanently closed except when charging or decharging. The basic tank is formed as a double-jacket structure. The electrolyte is heated over a high-temperature resistant oil within these double walls. The electrolyte can be filtered continuously through a pumping system located outside the plating equipment. Inside the air-lock is a rinsing device using toluene as a solvent for removal of excess electrolyte before taking finished parts out of the bath.

Because of the inflammability of the electrolyte system, all electric devices are constructed in an explosion-proof condition. Rapid air exchange within the whole facility and good gas tightness of the whole equipment prevent the cumulation of combustible or even such concentrations of organic compounds which are injurious to health. The maximum working concentrations can be held within the demanded limit during all stages of processing. No critical situation has occured within four years of continuous 24-hour work with this equipment.

The electrical generator provides DC, AC or periodic reverse currents of the demanded voltage and impulse form. Rectangular impulses can be produced with various energy content cathodically as well as anodically.

The equipment is suitable for coating parts of up to 400x400x450 mm. By use of an inner anode, complicated structures like tubes can be aluminated on the inner as well as on the outer surface.

1.5 Process Parameters

The general process parameters are summarized in Table 2. The choice of exact current density and deposition time mainly depends on the geometry of the part to be coated. Since the electrical conductivity of the nonaqueous electrolyte system is limited by the relatively small number of large organic complex ions, the throwing power of the electrolyte is relatively low and can be compared with that of chromic acid containing chromium electrolytes. Therefore, the thickness distribution on complicated structures varies within a large range.

A minimum thickness that will be a sufficient protection against corrosion is achieved by the following means:

- increasing the deposition time up to a value, where the minimum thickness can be guaranteed even at the most unfavourable point. This method will be applicable only, when the increased thickness on those coated surface sections, which can be coated more easily, does not affect the function of the part (e.g. on fasteners, in the thread of which too thick a deposit cannot be tolerated)
- deposit at low current density and increased time. At low current densities the throwing power is better, because more time is available for the limiting diffusion process to transport aluminium ions to the electrically "more remote" places
- use of assistant electrodes to provide sufficient ion flow to the remote surfaces. The aluminium electrodes work as additional anodes and are located at places coating of which is difficult, for instance blind holes, sharp corners etc.

A similar levelling effect can be achieved by the use of alternating current. The cathodic impulse intensity must always be greater than that of the anode, otherwise no deposition is possible. It has been shown (6) that the use of rectangular impulses gives the best results. Fig. 4 shows the principle of this process.

When using pure cathodic direct current or impulse a very non-uniform thickness distribution will be achieved (4a,b). The flux lines are cumulated on the male parts and their intensity is reduced on the female parts of the structure. The effect resulting is shown in the Figure 4b. The use of alternating impulses (4c) leads to a levelling effect (4d), the thickness differences are reduced. This is due to the effect, that the short anodic impulses attack in particular the male parts and reduce the thickness at these spots.

By use of the discussed electrolyte system, aluminium can be deposited principally on all materials with a certain electrical conductivity. Nonmetallic materials must be coated with a conductive layer before applying aluminium. For coating metallic parts two methods are used preferably

- preteatment is performed completely in the nonaqueous stage
- preteatment starts with the usual aqueous systems (e.g. alkaline degreasing, etching) and ends with the removal of the water by rinsing with organic solvents.

The second process has rather a limited field of application and is not applicable to the materials being most important for the aircraft industry, such as high-strength steels, and lightweight metals, like titanium, aluminium and their alloys. Highstrength steels, in particular with a strength above 1550 $N/mm^2$ must not be coated with aqueous electrolytes because of the danger of hydrogen embrittlement. Aluminium and titanium alloys form very stable surface oxide films. These films can be removed by etching (alkaline solutions for aluminium, nitric-fluorine acid for titanium), but reform rapidly when rinsing or transferring the parts to the coating bath. The thickness of the reformed oxide films is small enough to provide sufficiant coating, but no good adhesion will be achieved by this procedure.

Using nonaqueous pretreatment is quite a more promising way. The resulting adhesion is comparable with the values achieved by vacuum deposition (between 20 to 80 $N/mm^2$) in case of low- and high-strength steels. Aluminium and titanium alloys can be coated, but promise average adhesion only for the moment because of the extremely high oxide reforming rate. Our present equipment does not allow to work completely under purified nitrogen. We must proceed from one step to the next where the contact with air cannot be excluded (see Fig. 2). Our next "production scale" facility which is planned will give some improvements in this matter.

We think that the adhesion achievable at present is already sufficient for most purposes. The values of about 20 $N/mm^2$ are as compared with vacuum deposition, ion vapor deposition, chemical conversion coatings and organic resin layers.

The nonaqueous pretreatment consists of the following general steps:

- sandblasting of highly contaminated parts
- slurry blasting with a nonaqueous mixture of an abrasive material in an organic solvent. Oxide layers are removed by means of this process. Their reformation is hindered by the organic mixture which protects the surface up to the next cleaning step
- removal of the slurry in freon or perchloroethylene under ultrasonic application
- treatment in freon or perchloroethylene vapour. The transfer time of the parts from this to the next step is critical because - in particular when using perchloroethylene - the parts will become dry and reforming of oxide starts. As has already been stated, working completely under inertgas would prevent this undesirable effect
- rinsing in xylene to remove possible remainders of halogen containing compounds, which would cause damaging anodic side reactions
- rinsing in toluene
- transformation to aluminium electro-plating cell and start of coating.

This pretreatment can be modified for special purposes, but the line shown will be the same in general.

### 1.6 Anodic oxidation of electro-plated aluminium

By application of the commonly used anodizing processes,electrochemically deposited aluminium can be transformed into a very hard and abrasion-resistant structure. It is a well-known fact that the good resistance of aluminium against most environmental attacks is obtained by the formation of tight, highly adhesive layers of aluminium oxide. By an anodic process, using the aluminium part as the anode in an electrolyte system (e.g. solutions of sulfuric acid, chromic acid, phosphoric acid), this oxide layer can be thickened up to between 3 and 70 $\mu m$, according to the various well-known anodizing processes.

In our investigations, we have studied three different types of anodizing processes:

- dc-sulfuric acid anodizing,
- hard anodizing,
- chromate anodizing.

The important process parameters are listed in Table 3. The coatings were applied on sheet material, fasteners and tubes. The anodized specimens were tested for corrosion resistance, contact corrosion behaviour, thickness distribution, abrasion resistance and adhesion to the substrate.

### 1.7 Chromate Treatment

For better corrosion resistance, aluminium-coated specimens were treated with commercially available chromate solutions (Yellow Chromate Treatment BN 29492, Alodine 1200). Chemical composition and process parameters are listed in Table 4. By application of these chemical conversion coatings, electrochemically active protective layers of chromate compounds are produced on the aluminium surface.

## 2. High-Strength Steels

### 2.1 General

In general high-strenght steels (1) have a low alloy content (there is above all a lack of chromium). They are therefore very sensitive to various forms of corrosion. Being materials of very high importance for various industrial applications, they must be coated with suitable layers of anti-corrosive agents. As has been stated before, the use of aqueous processes (particulary cadmium electro-plating) cannot be tolerated. In the case of aqueous electro-plating, the codeposition of hydrogen is mostly inevitable. The very

small diameter of the hydrogen atom favours it's penetration into the metallic lattice. Hydrogen becomes a part of the lattice and can diffuse to imperfect places of the lattice. At such points (for exemple crack tips, grain boundary , lattice defects ), two hydrogen atoms reunite and form a hydrogen molecule (H2). This hydrogen molecule has a definite vapour pressure which can become very high in the limited space available. Therefrom result very high internal pressures (values up to 2400 bars have been observed). These pressures cause cracks and destroy the metal.

To avoid hydrogen embrittlement, innumerable process modifications and specifications have been developed, e.g.

- outgassing within a limited time after deposition
- coating with porous layers to favour the outgassing of hydrogen
- coating with cadmium or zinc layers containing certain amounts of titanium which is a very strong getter material for hydrogen
- use of a special pretreatment and of processes by which "no hydrogen is codeposited" or "the deposited hydrogen is in an non-dangerous form".

Some of these processes may be applicable for not too critical purposes. In general however, only absolute hydrogen-free deposition methods can be tolerated.

A promising way is the coating by vapour deposition or ion plating. Cadmium and aluminium can be applied by methods working with or without an electric field. The ion-vapour deposition (IVD) of aluminium has become an industrially applicable process within the last years (14,15). All technical processes have advantages and disadvantages, and the vapour deposition process has the following characteristics limiting its application:

- the deposition work must be performed in a chamber which is very highly evacuated.The equipment required to produce and provide a vacuum of the demanded properties is very expensive
- the adhesion of vapour deposited layers is limited in general. No exact data have been reported up to now
- coating of the inner surface of small tubes is, as far as we know, not possible; the throwing power of the process is very limited. The application of "assistant electrodes" is very complicated and in most cases impossible
- the density and pore-free state of the applied layers cannot be guaranteed. It is known that layers applied by vapour deposition have a structure oriented rectangularly to the surface. This orientation favours the penetration of corrosive chemicals to the basic material (salt water, humidity, sulfur dioxide containing gas).

It is one great advantage of vapour deposition processes that a large number of alloy combinations can be applied.

Besides the above described vapour-deposition process, coatings are used which are based on ceramic or organic resin systems containing aluminium. These systems are applied by painting, spraying or dipping. We have studied the protection against corrosion of some of these materials and have compared the result with our nonaqueous complex electrolyte system (1), see paras. 2.2 to 2.4.

## 2.2 Comparison of coating systems containing aluminium

### 2.2.1 Substrates and coatings

Substrates: (chemical composition see Table 5)

- precipitation-hardening steel PH 138Mo
- martensite-hardening steel Ultrafort 301
- low alloy steel (LN 1.7734)
- carbon steel 70Si7

The test specimens were cylindrical tube sections with a diameter of about 60 mm and cylindrical compact probes,

Coatings:

- aluminium deposited by means of the Siemens process, 30 to 50 µm
- ceramic layer containing aluminium, sprayed and heat-treated (300 to 550°C) 30 to 40 µm
- organic resin containing aluminium applied by dipping or painting, 5 to 15 µm.

### 2.2.2 Corrosion testing procedures

The following testing methods were used for the investigation of the corrosion behaviour of the coated specimens.

- salt immersion test under load (modified according to MIL.), cylindrical probes were tested under a preload of 0.8 $\sigma_{0.2}$ in the following medium.

| | |
|---|---|
| NaCl | 3.5 % per weight |
| pH | 6.5 |
| temperature | 25 ± 2° C |
| time | 240 hours |

The salt containing solution was circulated at a rate of 1 to 2 ml per 80 $cm^2$ surface and hour to avoid ageing effects within the solution.

- 100% relative humidity according to DIN 50017 or MIL cylindrical parts unloaded
- periodic salt immersion test under stress corrosion conditions (comparable to DIN 50908 or 51301, smooth cylindrical specimens were preloaded by use of a standardized ring).

The test conditions were

| | | |
|---|---|---|
| NaCl | 3.5 % per weight | |
| preload | 0.9 ± 0.2 | |
| immersion cycle | dipping time | 10 minutes |
| | exposure to air | 50 minutes |

2.2.3 Test results

The results of the investigation are summarized in Table 6. The corrosion behaviour is classified as follows:

1 - very good
2 - good
3 - satisfactory
4 - unsufficient

Aluminium coating

The corrosion-resistant quality of electro-plated aluminium varies from good to very good according to the applied test method. Corrosion was observed to a very limited extent. The total number of corrosion pits, red corrosion products and surface corrosion was very small. Delamination of large surface areas was observed in no case. The adhesion of the aluminium coating on the substrate was very good. Fig. 5 shows a micrograph of an aluminium coated steel specimen (1.7734) after salt spray testing. The aluminium layer has a very dense structure which is free from pores. No inclusions in the interface and no signs of delamination are visible.

The mechanical properties (stress, strain) of aluminium-coated steel 1.7734 are not influenced by the coating. This could be shown clearly by stress tests performed after corrosion treatment. The stress and strain properties of aluminated material were only slightly different, compared with the original material. Of the aluminium-coated specimens. 100 % survived the alternating salt immersion test, of the uncoated specimens none. This gives good evidence of the protective properties of the aluminium layer.

Ceramic coating

The resistance to corrosion of aluminium-containing ceramic material varies from very good to good and is comparable with the electro-plated aluminium coating (Table 6). The percentage of corrosion was very low. Only a limited amount of red-brown corrosion products and some pits could be observed on the surface. The micrograph in Fig. 6 shows a ceramic coating on a steel substrate (Ultrafort 301) after salt-spray-testing. Some pores and holes are visible on the layer and may cause corrosion under severe environmental conditions. Probably, these imperfections are the product of dipping, painting or heat treatment operations. Compared with aluminium coating applied by means of electrodeposition, the ceramic layer appears to be of a less dense strucure.

In addition, the application temperature of the ceramic layer is very high. When coating sensitive materials, there is a serious danger of deterioration of the material properties.

Organic coating

The corrosion resistance of the investigated organic coatings (two different systems were studied) to humidity is good. Under salt-spray conditions, the behaviour was very bad (Table 6). The total amount of corrosion was very high (red-brown corrosion products, large surface delaminations). Fig. 7 shows the aluminium-containing organic resin layer on the Ultrafort 301 steel substrate after the salt-spray test.

The coating has been attacked very seriously and can no longer protect the basic material very effectively. The incorporated aluminium particles will provide only limited cathodic protection because of the electrically insulating properties of the surrounding resin.

The good resistance to humidity is evidently obtained due to the water-resisting quality of the organic resin.

In general, the protection by means of organic systems is less effective, compared to metallic or metal-containing coatings. One of the additional disadvantages of the investigated organic coatings is due to the fact that the layer thickness was much lower (5 to 15 µm) compared with the ceramic and electro-plated systems (40 to 50 µm)

2.3 Corrosion and contact-corrosion testing

To determine the corrosion behaviour of aluminium deposits alone and in contact with usual structure materials, a number of threads, plates and tubes was coated with aluminium and tested in salt-spray and humidity environments. The experimental results of coated sheet material are summarized in Tables 7 to 8.

It could be shown that all coatings (pure aluminium, chromate conversion coatings, hard anodized layer, chromic-acid anodizing, direct-current sulfuric acid anodizing) were resistant to corrosion under salt-spray and humidity conditions. The pure aluminium layer was covered with white corrosion products, which is to be expected on coatings with sacrificial anode behaviour.

## 3. Properties of a aluminium-plated steels

By coating steels with electro-deposited aluminium, certain physical or chemical properties of the resulting compound are or may be different from the previous state. In the next chapters, the following parameters will be discussed, based on experimental results

- internal strains of electro-plated aluminium
- adhesion of aluminium deposits
- abrasive resistance of anodized aluminium
- fatigue life of steel parts coated with electro-plated aluminium
- stick slip behaviour of aluminium-coated fasteners.

In addition, a comparison between anodic coatings and hard chromium layers is made with respect to fatigue life, abrasive resistance and influence on the basic material properties.

### 3.1 Internal strains

Good adhesion of the electro-plated metals on the substrate is most important for resistance to corrosion and fatigue life of the coated parts. Internal strains in the deposit may cause a reduction of the useful lifetime of the coated part because of bad adhesion, delamination of the coating and higher susceptibility to stress corrosion.

Bad adhesion is influenced mainly by the occurrence of stress forces in the interface. They are caused by various factors like influence of the structure of the substrate, incorporation of contaminations into the metallic deposit. The incorporation of organic additives, such as brighteners and levelling agents may be a hindrance to sliding motions of lattice interfaces and cause internal stresses.

Therefore, it is very important to guarantee a low stress level in the deposited metallic layer.

Aluminium deposited out of the nonaqueous organic complex electrolyte is extremely pure and by adequate processing practically free of contaminants. The electro-plating mechanism produces a very fine, non-orientated grain structure without considerable tensions or lattice imperfections. Therefore, the metallic aluminium is supposed to have a very low level of internal stresses. This could be stated by strain measurements using the X-ray diffraction method.

This method is based on the fact that internal stresses cause changes in the lattice distance of the crystalline metallic structures. Therefrom results a change of the reflection angle of X-rays compared with the non-stressed material.

Internal tensile stresses within the range of - 30 $N/mm^2$ could be measured by using the X-ray diffraction method. This stress level is by far too low to have any influence on the adhesion properties of aluminium.

### 3.2 Adhesion of aluminium deposits

Good adhesion of metallic deposits on the substrate mainly depends on the following facts:

- the surface of the substrate must be absolutely free of contaminants, like grease, oils, residual oxide layers and imperfect crystalline structures (the latter being caused by mechanical milling)
- the growth of the metallic deposit must start from as much locations as possible, good activation is therefore extremely important
- roughening of the substrate surface by mechanical means, like sand blasting, increases the active surface and therefore gives better adhesion. Probably, mechanical linking provides an additional improvement
- the pretreatment should rather be chemical than mechanical, at least during the last step before coating. Mechanical polishing has the disadvantages of contamination by abrasives, deterioration of the surface grain structure and formation of oxide layers by overheating
- the crystal structure of the substrate should, within certain limits, be similar to that of the coating to guarantee identical structural growth of the metallic deposit on the substrates
- alloying between substrate and coating leads to better adhesion. Because of the low working temperatures of most electro-plating solutions, this effect is probably not very important. The formation of alloys on the interface may be favoured by a thermal posttreatment in some cases
- as had already been stated, the influence of internal stresses within the electrodeposit is very important. These stresses favour the occurrence of shear forces in the interface.

The adhesion of metallic deposits can be measured by various means (9,10). A testing procedure has been developed in the last years to determine the exact adhesion values of various coating-substrate systems (11,12). The principle of this process is shown in Fig. 20.

A cylindrical probe is mechanically milled (20a), coated with the deposit to be investigated (20b), strengthened with a thick copper or nickel layer (20c) and milled to the final form (20d). This specimen is tensile-tested by use of a stamp, the thick nickel layer avoids the occurrence of shear forces at the substrate-coating interface. Due to the knowledge of applied force and interface area, the exact adhesion value can be calculated.

This method allowed to estimate the adhesion of electro-plated aluminium on various substrates. Table 12 gives a summary of investigated systems, coating procedures and adhesion values achieved.

Owing to the use of intermediate layers, the adhesion properties are quite sufficient. The application of the slurry blasting process is much more difficult and the investigation of this system has been started just a short time before this publication. Therefore, no statistically secured data can be given today.

In addition to the standard probes, some more testing procedures (shear and peel tests, scratch tests, heat treatment, deep drawing test) were investigated. They all stated the fact that the aluminium layer could be applied very tightly and with good adhesion to the steel substrate.

### 3.3 Abrasion Resistance

By anodic oxidation, the soft aluminium layer can be transformed into a hard and abrasion-resistant aluminium oxide layer. The micro-hardness increases from 20 . 10 N/mm$^2$ (pure electro-deposited aluminium) to more than 400 x 10 N/mm$^2$ (oxide layer) (8).

The resistance to abrasion depends on various parameters, such as hardness, ductility, freedom of cracks and incorporations, good adhesion on the substrate. Too hard a layer may show brittle properties and,therefore, decrease the abrasion resistance. Cracks in the deposit as, for example in the case of hard chromium, may be a limitation instead of maximum hardness. Bad adhesion may lead to local surface delaminations and cause undesirable fretting corrosion and thus deterioration.

The abrasion resistance of oxide layers produced by various anodizing processes was investigated by using a Taber Abraser similar to equipment according to ASTM D 1242 - 64 or DIN 53754, DIN 53799. The abrasive rolls were of the CS-17 type, the load applied was 100 g, the specimes were plates of the dimensions of 110 x 110 x 2 mm. The abrasion rate was estimated by determining the loss in weight in a certain number of cycles. To obtain a rough comparison between oxide layers and hard-chromium coatings under strictly slip abrasion conditions (no impact tests were performed), the latter were tested according to the same procedure. The process parameters and testing results are summarized in Table 13. It could be shown that the abrasion resistance of hard-anodized aluminium coatings is up to 10.000 rpm at least within the range of hard-chromium deposits. Anodized aluminium, therefore, seems to be a suitable material for the replacement of hard chromium layers in some fields of application. Compared with electro-plated chromium, it has the additional advantages that the layers do not involve the danger of degradation of the basic material, e.g., by hydrogen embrittlement. Compared with the abrasion behaviour of hard-anodized aluminium alloys, the oxide layer on pure electro-plated aluminium seems to be more stable. This is probably due to a lack of impurities which may cause the formation of weak mixed oxide structures.

### 3.4 Fatigue life

To investigate the influence of electro-plated aluminium on the mechanical properties of the steel substrate, a study of the behaviour under cyclic load was necessary. Two different testing methods were applied:

- reverse bending tests of a cylindrical specimen to establish stress-cycles to failure (according to DIN 50113). This test causes an extreme strain of the surface sections and is therefore a good method for the investigation of coating influences. The tested material was steel 1.7734.6 (tensile strength 1160 N/mm, Vickers hardness 364 x 10 N/mm$^2$).
- cyclic load testing was performed on fasteners of high-strength steel 1.7784.5.

The specimens for both testing procedures were coated with aluminium by electro-plating. A part of the specimenswas anodized after the deposition of aluminium.

To compare the influence of aluminium coating with hard chromium, a fatigue curve of chromium-coated material was established additionally, The deposition of chromium was performed by using the standard chromium electrolyte (chromic acid solution containing one percent by weight of sulfuric acid). Degassing of the specimen was performed immediately after the chromium-deposition.

#### 3.4.1 Reverse bending tests

The following different surface preparations were studied:

A - mechanically milled
B - mechanically milled and slurry blasted (non-aquous system)
C - mechanically milled,slurry blasted and electro-plated with aluminium (20 to 30 µm)
D - mechanically milled, slurry blasted, electroplated with aluminium (20 to 30 µm) and dc-sulfuric acid anodized (15 µm)
E - mechanically milled, coated with hard chromium, degassed.

The test was performed according to DIN 50113 using a reverse bending test machine, type "Punz" (Schenk, FRG), in normal air with a frequency of 6000 CPM. The applied stress levels were chosen to achieve failure within $10^7$ cycles. Those specimens, which had passed the test without faulure, were subjected to a higher stress and tested again.

The processing parameters and testing results are summarized in Table 14. The stress fatigue of the studied systems are shown in Fig. 21.

The results confirmed the fact that the aluminium coating has no detrimental effect on the material properties of the substrate. The fatigue life of the mechanically milled and untreated (A), slurry blasted (B) and aluminium coated (C) specimens lies in the same range. The anodized coating could not withstand the severe attack on the surface and delaminated within a short time. The lifetime of the basic material was not influenced by this process, the soft aluminium interface probably being a hindrance to crack propagation. Under normal conditions, the occurrence of such severe stresses is not usual.

The hard-chromium layer (E) reduced the fatigue life extremely, the substrate is considerably influenced by this deposit.
This is a well-known fact, as the surface of hard-chromium layers shows a fine microcrack structure.

### 3.4.2 Cyclic load testing

Fasteners of high-strength steel 1.7784.5 were tested under the following conditions:

Coatings:

- electro-deposited aluminium, non aqueous pretreatment, aluminium thickness 6 µm
- vapour-deposited cadmium 7,5 to 10 µm
- uncoated specimen

Test conditions:

- cyclic load testing under constant stress
- lubricant Tiolube 460
- stress levels (A) 200 N maximum
  80 N minimum
  (B) 1210 N maximum
  710 N minimum
- tested in connection with 1.4944.

The parameters of test A were according to LN 65013. Test B was performed using different stress levels. This was necessary because, under the conditions of LN 65013, no failure could be initiated. By increasing the applied stress levels, failure occurred within the time fatigue resistance range (Table 15). Therefore, the comparison of the test results is somewhat difficult. The following conclusions could be drawn:

- the quality of the aluminium coating under cyclic load is fully in accordance with the requirements of LN 65013
- the mechanical properties of the substrate are not affected by the aluminium coating under the applied cyclic load levels. The testing in connection with the 1.4944 screw shows this quite clearly. The achieved endurance number lies considerably above the specified level of $0.65 \cdot 10^5$. The fracture was not observed in the screw, but in the shaft region, and it was not caused by material fatigue, but by fretting corrosion
- compared with the uncoated material, the cadmium layer caused a considerable decrease of the endurance.

As has been stated, the various tests are not quite comparable. They were made in different studies and for different purposes. However it could be stated very clearly that the electro-deposited aluminium has no detrimental influence on the properties of the basic material.

### 3.5 Coefficient of friction

The coefficient of friction is of high importance for bolted connections. A small friction coefficient requires only small forces to fasten with the screw in order to obtain a high initial load (pre-stress). Severe damage of the surface loyer is not be expected out of this reason.

By testing 1.7794.5 threads, coated with 6 µm electro-plated aluminium, lubrified with Tiolube 460 in connection with 1.4944 the coefficient of friction was extremely low and the scatter band very tight between 0,07 to 0,10 µ in five successive tests. Testing without lubricant resulted in coefficients of friction decreasing from 0.16 to 0.10 µ.
This effect is caused probably by a smoothening effect of the soft aluminium layer. No seizing up was observed with or without lubricant.
Additional protection reduces the attack by corrosion, and the layers become much more resistant against environmental influences.

### 3.6 Corrosion resistance

A number of fasteners was tested under salt-spray conditions according to MIL-STD 810C or DIN 50021. The applied coating systems proved well adherent and gave a tight and pore-free surface conditions.

The thickness distribution of the aluminium-coated fasteners varied between 10 and 30 µm (Fig. 8) and between 5 and 15 µm (Fig. 9) for the thin layers.

Vapour-deposited cadmium was applied in the 7.5 to 10 µm thickness range. The following systems were studied:

- 1.7784, coated with aluminium (minimum thickness 5 µm)
- 1.7784, aluminium 10 µm minimum, 2 - 3 µm dc-sulfuric acid anodizing
- 1.7784, aluminium 10 µm minimum, chromate treatment
- 1.7784, vapour-deposited cadmium 7,5 - 10 µm
- 1.7784, uncoated.

The cadmium-coated as well as the aluminium-coated, chromate-treated and anodized fasteners showed no signs of relevant attack by corrosion after a testing time of 100 hours. Fig. 10 and 11 show specimens anodized by dc-sulfuric acid as well as uncoated specimens before and after the salt-spray test. Compared with the uncoated material, anodizing provides a very good resistance to corrosion. Chromate-treated aluminium coatings before and after salt-spray testing are shown in Fig. 12. The influence of the protective coating is obvious. Anodized coatings after humidity testing are shown in Fig. 13. The influence of salt-spray testing on cadmium-coated fasteners can be seen in Fig. 14.

It is important that even the very thin aluminium layers showed sufficient protection against corrosion. By application of thin oxide layers (2 - 3 µm), a highly improved resistance can be achieved.

By use of an assistant electrode, tubes of 1.7734 high-strength steel were completely coated with a corrosion- and abrasion-resistant layer of 100 µm aluminium and a layer of 20 - 25 µm anodized by dc-sulfuric acid. Salt-spray testing (96 hours, MIL-STD 810 C, DIN 50021) showed no visible signs of attack by corrosion. Similar results were achieved with aluminium-coated and chromate-treated tubes (Fig. 15).

The contact-corrosion behaviour was investigated according to the following procedure. High-strenght fasteners were coated with various surface protection systems, fixed in an aluminium-alloy block and tested under salt-spray and humidity conditions. The important process parameters are summarized in Table 9. The experimental results are given in Tables 10 and 11.

The tests showed that all surface layers (electro-deposited aluminium with and without additional chromate treatment, anodized aluminium, vapour-deposited cadmium) provided good protection qualities. The results of 100 hours salt-spray treatment are shown in Fig. 16 and 17. The aluminium-coated, anodized and chromate-treated fasteners showed no signs of corrosion on the head as well as on the shaft. The sections having been in direct contact with the aluminium block, showed no signs of corrosion at all. The aluminium block was covered with white corrosion products on the surface, but no signs of corrosion were observed on spots having been in contact with the coated fasteners.

Cadmium-coating, too, showed good protection properties in salt-spray and humidity environments. Fig. 18 and 19 show uncoated and cadmium-coated fasteners (1.7784) after 20 cycles of humidity testing. The uncoated specimen was corroded severely, the cadmium-coated fastener showed good corrosion resistance.

The investigations have clearly shown that aluminium coatings, applied by an electrochemical deposition process, are comparable with the usually applied cadmium coatings under several environmental conditions. Taking into account the additional advantages of aluminium

- deposition on an economic scale - no danger of environmental intoxication - (aluminium coatings will be between 30 and 50 % more expensive than aqueous platings, but are much cheaper compared with vapour-deposited coatings);
  aluminium coatings will be a very good subsitute for the demanded replacement of cadmium.

## 4. Light weight materials

### 4.1. Aluminium Alloys

High-strength aluminium alloys, e.g., 2024 or 7076, sometimes present corrosion problems because of the content of alloying elements like copper. Therefore, in some aircraft structures, aluminium coated aluminium alloy sheets are used to provide sufficient corrosion properties.
Mechanically milled components, such as stringers or fittings, have rather a complicated structure and cannot be coated by mechnical means. Coating with aluminium by electroplating seems to be a very promising method to provide comparable prodection of these parts.

The protection of aluminium alloys by anodizing is possible too, but has some disadvantage

- the fatigue life of anodized parts is reduced because of the brittleness of the oxide layer favouring crack propagation,
- the application of modern procedures for increasing the useful lifetime of structure-fastener combinations is not possible by using anodizing methods,
- pores in the oxide layer cause a severe attack by corrosion, because the oxide layer has no sacrifical anode properties,
- the milling of holes is performed after anodizing. Therefore, no protection by thick oxide layers is possible inside the holes.

Some investigation programmes are performed to provide good adhesion of electro-plated aluminium on aluminium alloys. The most important hindrance for a tight connection between substrate and coating is the oxide layer which is electrically non-conductive and prevents good adhesion.

By application of the non-aqueous slurry blasting process, this limitation might be overcome. The reformation of oxide layers can be avoided very effectively by using this form of pretreatment.

### 4.2 Titanium alloys

Coating of titanium with aluminium might be of interest for the following reasons:

- titanium fasteners cause damage due to contact corrosion when used in aluminium structures because of the nobler behaviour of titanium in electrochemical respect
- anodizing of the aluminium structure is not possible, because the holes are drilled after anodizing the complete part
- coating of titanium alloys with cadmium is prohibited because of the danger of solid cadmium embrittlement (13)
- titanium is very sensitive to fretting corrosion. Critical metal combinations are coated with silver by a very expensive process. Coating with aluminium might provide a good replacement.

Coating of titanium alloys with electro-deposited aluminium is intensively studied in a complex investigation programme.

The problems of achieving good adhesion are very similar to those of aluminium alloys. Nonaqueous slurry blasting seems to be a very promising process to solve the adhesion problem.

### 4.3 Magnesium alloys

Owing to their low density and good mechanical properties, magnesium and its alloys are of interest for certain military aircraft and space applications.

Their resistance to corrosion is bad, compared with aluminium and titanium. No tightly adherent oxide layers can be formed on magnesium.

The protective coatings used, such as chromate treatment plus organic-resin painting or anodizing processes, have some serious disadvantages.

Pure aluminium may provide a corrosion-resistant layer on magnesium. Being nobler in the electrochemical potential series than the magnesium substrate, there might arise a corrosion problem on mechanically damaged surface areas.

The anodized layers and paintings suffer from the same disadvantage having no sacrifical anode behaviour in this case. Therefore, aluminium coatings may be used to replace these protection methods. Investigations in these field are under way.

### 4.4 Fibre reinforced metals

By embedding high-strength fibre materials, e.g., boron fibres, extremely high-strength and lightweigth composites can be produced. Possible fields of application of these exotic materials are found in the space and aircraft industry, where pressure vessels and combustion chambers might be produced by means of this technique.

Present investigations clearly demonstrate the applicability of the aluminium electrodeposition process for the production of fibre reinforced aluminium structures. Thick aluminium layers can be deposited by means of this process. The fibres are coated and embedded completely, and tight, pore-free structures are achieved. Cylindrical aluminium parts with a fibre content of approximately 35 % by volume were produced and burst-pressure tested. The average tensile strength of the composite was calculated to be 900 $N/mm^2$, at a density of 2,5 $g/cm^3$. These results seem to be very promising, and further investigations are planned to produce an extremely lightweight pressure vessel for space applications (16).

## 5. Conclusions

The investigations described have shown that electro-desposited aluminium is a suitable protective coating for various aircraft and space applications. The metal can be deposited in a very high purity and forms pore-free, tightly adherent surface layers. Various substrates, such as high-strength steels, aluminium, magnesium, titanium and their alloys, can be coated. Since deposition is performed in a nonaqueous electrolyte, there is no danger of hydrogen embrittlement of high-strength steels and hydrogen-sensitive materials.

The layers applied provide good protection against corrosion under various environmental conditions. The influence of salt-spray, humidity, cyclic and static load and contact corrosion has been investigated within the scope of our studies. The fatigue life of high-strength steels was not reduced by the aluminium coating applied.

The electro-plated aluminium can be anodized by various processes (sulfuric acid d.c. anodizing, hard anodizing, chromic acid anodizing) resulting in a very hard and abrasion resistant surface. We have thus succeeded in achieving an advantage as compared with usually applied coating systems, e.g. cadmium. In addition to this fact, aluminium is a nontoxic material compared with the highly toxic and environmentally dangerous cadmium. Any contamination of the environment by waste products will thus be avoided.

| Electrolyte system | Process Parameters |
|---|---|
| $AlCl_3$ in ethylpyridiniumbromide and toluol | 25-30°C. 1A/dm$^2$, c.c.e 85 % |
| $AlCl_3$ in etheric solution | 1-10 A/dm$^2$ |
| $AlBr_3$ in ethylbenzene | room temperature |
| $AlCl_3$ (n-Propylbenzene)-(Di-n-Propylether) + $LiAlH_4$ (Kumol Diethylether) | 40°C, 15 A/dm$^2$ |
| $AlCl_3$ $LiAlH_4$ in THF | 10°C, 1 A/dm$^2$ |
| $AlCl_3$ LiH in etheric solution | SA 100 % |
| Grignard-solution of aluminium und ethylbromide in Benzene (Diethylaluminiumbromide and ethylaluminiumbromide) | 0,5 - 2 A/dm$^2$ 50 % c. c. e |
| 75 % p.w. $Na_3AlF6$ + 25% p.w. $NaF$ + $Al_2O3$ | 1000°C, 15 A/dm$^2$ |
| NaCl, KCl, $Na_3AlF_6$ salt melt solution | 7-800°C, 10 A/dm$^2$ |
| mixture of alkaline and alkaline earth metals fluorides, containing aluminium fluoride | min. 600°C max. 10 A/dm$^2$ |
| $AlCl_3$, NaCl salt melt solution | containing hydrogen ions 140-280°C |
| $AlCl_3$, Na(K)Cl salt melt solution | 2-10 A/dm$^2$periodic reverse anod. 1-10", kath. 10-15" |
| $NaAl(C_2H_5)Cl_3$ + $C_2H_5Cl$ | 55°C, 12 V 0,8 A/dm$^2$ |
| NaF . 2 $Al(C_2H_5)_3$ in toluene 1 : 1 | 80-90°C, 0,8 A/dm$^2$ |
| Aluminiumalkylcomplex solution in toluene | 80-90°C, 3 - 10 V 2 A/dm$^2$ |

Table 1: Systems for the electro-deposition of aluminium(1)

| | |
|---|---|
| Chemical composition | 2 Al $(C_2H_5)_3$ - x NaF + 3,35 m $C_6H_5$ $CH_3$ |
| el. conductivity | (0,5 - 1,5) - $10^{-2}$ $\Omega^{-1}$ cm |
| process temperature | 80 - 95°C |
| current density | 0,5 - 5 A/dm$^2$ |
| deposite rate | 10 - 20 µm/hour on average |
| thickness of layer | in the µm to mm range |
| current form | direct current (dc) or dc with super alternating current (ac) |
| impulse form | rectangular impulses, periodic reverse possible |
| stirring of bath | by continuous filtration or movement of parts |
| anode material | pure aluminium |
| preatreatment | nonaqueous or aqueous with transformation to non-aqueous system |
| posttreatment | anodizing, colouring, glass peening, chromate treatment, electropolishing |
| basic materials | all conductive materials |

Table 2: Composition and process parameters of Siemens electrolyte (1)

| | dc-sulfuric acid | hard anodize | chromic acid anodize |
|---|---|---|---|
| bath concentration | 18% p.w. sulfuric acid | 130g/l sulfuric acid | 30-40g/l chromic acid |
| process temp. | 18°C | 13g/loxalic acid 0 - 5°C | 18° C |
| applied voltage | 16 - 17 V | increasing to 120 C | increasing to 50 V |
| process time | 15 min. | - | 40 min. |
| current density | - | 0,5-4A/dm$^2$ | 0,7A/dm$^2$ |
| oxide layer thickness | 12 µm | 50 - 60 µm | 3 - 6 µm |

Table 3: Anodizing solutions - chemical composition and process parameters

| | | |
|---|---|---|
| | Alodine 1200 | Yellow Chromate BN 39 492 |
| concentration | 10g/l Alodine 1100 | 20g/l Chromat Solution |
| process temperature | 40°C | 30°C |
| process time | 4 min. | 1 min. |
| pretreatment | etching sodium hydroxide 3 sec.<br>etching nitric acid 3sec. | -<br>- |
| post-treatment | - | rinsing in cold water<br>rinsing in hot water<br>drying in air, 60°C |

Table 4: Chemical conversion coatings-chemical composition and process parameter

| Steel | Chemical Composition | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | Mn | Cr | Si | Mo | V | Ni | Co | Ti | Al |
| PH 138 Mo | ./.0,05 | ./.0,10 | 12,25<br>13,25 | ./.0,10 | 2.00<br>2,50 | -<br>- | 7,5<br>8,5 | -<br>- | -<br>- | 0,9<br>1,35 |
| Ultrafort 301 | 0,02 | - | - | - | - | - | 1,8 | 8,00 | 0,5 | - |
| 1.7734 | 0,13 | 0,80 | 1,25 | - | 0,80 | 0,20 | - | - | - | - |
| 70Si7 | 0,7 | 0,8 | - | 1,7 | - | - | - | - | - | - |
| 1.7784.5 | 0,40 | 0,29 | 4,95 | 0,91 | 1,28 | 0,47 | - | - | - | - |

Table 5: Chemical composition of high strength steels

| Test procedure | PH-13-8Mo | Ultrafort 301 | 1.7734 | 70 8[illegible] |
|---|---|---|---|---|
| salt-spray test | - | 2 | 2 | 2-3 |
| humidity test | - | 2 | 2 | 3 |
| periodic salt immersion test | 1 | - | 1 | - |
| salt-spray test | - | 1-2 | 1-2 | 1 |
| humidity test | - | 1 | 1-2 | 1 |
| salt-spray test | - | 4 | 3-4 | 2-4 |
| humidity test | - | 1-2 | 1-2 | 2 |

Table 6: corrosion behaviour of coated steels (1)

| Substrate | Coating | Testing time (hours) | Notes |
|---|---|---|---|
| Ultrafort 301 | 80µm aluminium chromate-treated | 96 | no surface corrosion, very limited local delaminations no attack on substrate |
| Ultrafort 301 | 80µm aluminium 50-60µm hard-anodized | 96 | no surface corrosion, very limited local delaminations no attack on substrate |
| Ultrafort 301 | uncoated | 96 | severe attack by corrosion |
| 1.7734.4 | 30-35µm aluminium Alodine 1200 | 48 to 96 | no attack by corrosion |
| 1.7734.4 | 80µm aluminium chromic acid anodized | 96 | no surface corrosion, no delamination (bubbles) |
| 1.7734.4 | 30-35µm aluminium 10-12µm dc-sulfuric acid anodized | 48 to 96 | no attack by corrosion slight corrosion on pores |
| 1.7734.4 | 3µm copper 80µm aluminium 25-30µm dc-sulfuric acid anodized | 96 | no surface corrosion limited local delaminations no attack on substrate |

Table 7: salt-spray testing of electro-deposited coatings (MIL STD 810c or DIN 50021, sheet material)

| Substrate | Coating | Testing time | Notes |
|---|---|---|---|
| Ultrafort 301 | 80µm aluminium 25-30µm dc-sulfuric acid anodized | 20 cycles of 24 hours | no surface corrosion |
| Ultrafort 301 | 80µm aluminium 50-60µm hard-anodized | -"- | no surface corrosion slight corrosion on a few pores |
| 1.7734.4 | 80µm aluminium | -"- | no surface corrosion |
| 1.7734.4 | 80µm aluminium chromate-treated | -"- | no surface corrosion |
| 1.7734.4 | 3µm copper 80µm aluminium 25-30µm dc-sulfuric acid anodized | -"- | no surface corrosion |
| 1.7734.4 | 80µm aluminium chromic acid anodized | -"- | no surface corrosion |
| 1.7734.4 | 80µm aluminium 50-60µm hard-anodized | -"- | no surface corrosion |
| 1.7734.4 | uncoated | -"- | severe attack by corrosion |

Table 8: Humidity testing of electro-deposited coatings (SFW DIN 50017) sheet material

| | |
|---|---|
| Contact material | 3.1354.6 (AlCuMg) |
| Screws and shims | 1.4944 stainless steel |
| Fasteners<br>M6, M 12x1,5, M14 | 1.7784 high-strength steel |
| twisting moments<br>in mKp | M 6 1,7<br>M 12 x 1,5 8,3<br>M 14 15 |
| coatings<br>(minimum thickness<br>in thread section | 10 µm aluminium<br>10 µm aluminium, 2 - 3 µm anodized<br>10 µm aluminium, chromate treated<br>7,5 - 10 µm vapour-deposited cadmium<br>uncoated |

Table 9: Contact corrosion tests - materials and coatings

| Substrate | minimum coating thickness | testing time (hours) | Notes |
|---|---|---|---|
| 1.7784 | 10 µm aluminium | 96 | no attack by corrosion |
| 1.7784 | 10 µm aluminium chromate treated | 96 | no attack by corrosion |
| 1.7784 | 10 µm aluminium Alodine 1200 | 96 | no attack by corrosion |
| 1.7784 | 10 µm aluminium 3 µm dc-sulfuric acid anodized | 96 | no attack by corrosion |
| 1.7784 | 7,5 - 10 µm vapour deposited cadmium | 96 | no attack by corrosion |
| 1.7784 | uncoated | 96 | severe attack by corrosion |
| 3.1354.6 | uncoated | 96 | attack by corrosion |

Table 10: Contact-corrosion testing under salt-spray conditions (MIL-STD 810C) - contact block 3.1354.6

| Substrate | minimum coating thickness | testing time | Notes |
|---|---|---|---|
| 1.7784 | 10 µm aluminium | 20 cycles | no corrosion |
| 1.7784 | 10 µm aluminium-chromate treated | 20 cycles | no corrosion |
| 1.7784 | 10 µm aluminium 3 µm dc-sulfuric acid anodized | 20 cycles | no corrosion on critical parts oxyde layer damaged in thread section |
| 1.7784 | 7,5 - 10 µm vapour-deposited cadmium | 20 cycles | no corrosion |
| 1.7784 | uncoated | 20 cycles | severe corrosion |
| 3.1354.6 | uncoated | 20 cycles | corrosion |

Table 11: Contact-corrosion testing - humidity DIN 50017 - conatct block 3.1354.6

| Test specimen | Process steps | Adhesion ($N/mm^2$) | Notes |
|---|---|---|---|
| 1.7734.4 | nonaqueous slurry-blasted 250 µm aluminium 2mm copper | - | - |
| 1.7734.4 | electro-plated copper (3 to 5 µm), electro-plated aluminium 250 µm, 2mm copper | 90 - 105 | cleavage on steel-gold interface |
| 1.7734.4 | electro-plated gold 1-3µm electro-plated aluminium 2 mm copper | 100 - 140 | cleavage in aluminium layer |

Table 12: Adhesion of electro-plated aluminium on 1.7734.4 steel substrate

| Coating system | Number of cycles (Upm) | Abrasion value (mg) |
|---|---|---|
| 80 µm aluminium<br>50 - 60 µm hard-anodized | 10.000 | 17 |
| 50 µm hard chromium, unpolished | 10.000 | 32 |
| 50 µm hard-chromium, polished | 10.000 | 23 |
| 80 µm aluminium<br>15 µm dc-sulfuric acid anodized | 1.000 | 28 |
| hard-anodized aluminium layer (reference standard) | 10.000 | 20 - 25 |

Table 13: Abrasion resistance of anodized and hard-chromium-plated 1.7734 steel

| surface | Code | fatigue limit ($N/mm^2$) | Notes |
|---|---|---|---|
| mechanically milled | A | 665 | reference standard |
| slurry-blasted | B | 680 | - |
| aluminium-coated | C | 660 | after breakage slight delamination of coating near fracture |
| anodized | D | 675 | oxide layer delaminated after short testing time, no influence on substrate properties |
| hard-chromium-coated | E | 300 | substrate strongly influenced by the chromium coating |

Table 14: Reverse bending tests of steel 1.7734.6 material(coated with different layers)

| Specimen | tension level (testing method) $N/mm^2$ | | endurance | Notes |
|---|---|---|---|---|
| 1.7784.5, 6 µm Al<br>Tiolube 460 | 800<br>80 | (A) | $0,49.10^5$ | fixture on thread<br>fracture in thread section |
| 1.7784.5, 6 µm Al<br>Tiolube 460 | 800<br>80 | (A) | $2,15.10^5$ | in screw 1.4944, fracture in the shaft region by fretting corrosion before time |
| 1 7784.5 uncoated | 1210<br>710 | (B) | $2,32.10^5$ | uncoated fastener in screw without lubricant |
| 1.7784.5 vapour deposited cadmium | 1210<br>710 | (B) | $0,45.10^5$ | inscrew without lubricant |

standard tensile strength (LN 65013) of 1.7784.5 1520 - 1670 $N/mm^2$
$\sigma_{0,2}$ 1370 $N/mm^2$

standard-endurance (n)(LN 65013) (A) $n = 0,65.10^5$

Table 15: fatigue tests under constant stress

## 6 References


/1/ W. Wittich, R. Suchentrunk, H. Kellerer
Metall 30 (1976), 10, 943 - 47

/2/ J.H. Couch, A. Brenner
A Hydride Bath for the Electro-deposition of Aluminium
J. Electrochem. Soc., vol. 99, no. 6, June 1952, 234 - 44

/3/ R. Benninghoff
Galvanotechnik 63 (1972), 4, 349

/4/ Joan B. Berkowitz, Newton H. Emerson
Plating Methods, NASA SP 5114, 1972

/5/ J.H. Connor, A. Brenner
Electrodeposition of Metals from Organic Solutions II Further Studies on the Electro-deposition of Aluminium from a Hydride Bath
J. Electrochem. Soc., vol. 103, no. 12, Dec. 1956, 657 - 62

/6/ R. Dötzer
Galvano-Aluminium und seine anodische Oxidation
Chemie-Ing. Technik 45 (1973), 653 - 58

/7/ R. Dötzer
Proceedings of the 9th world congress on Metal Finishing, Amsterdam, Netherlands
26 - 29. Oct. 1976 (non publicated presentation)

/8/ R. Dötzer
VDI - Berichte 309 (1978), 95 - 104

/9/ W. Dettner, J. Elze
Handbuch der Galvanotechnik 3, 504 - 12 (1963)

/10/ W. Riedel
Jahrbuch der Oberflächentechnik 163 - 67 (1978)

/11/ R. Suchentrunk
Grundlagen und Praxis der Haftung beim Beschichten und Verbinden
DGM Symposium, Bad Nauheim 1977

/12/ O. Tuscher, R. Suchentrunk
Galvanotechnik

/13/ D.N. Fager, W.F. Spurr
Corrosion Magazine 26 (1970), 10, 409 - 19

/14/ A.W. Morris
NACE Symposium, Houston, Texas 22. - 26.3.1976

/15/ E.R.Fannin , K.E.Steube
AIAA 16. Structures, Structural Dynamics and Materials
Denver, Colorado 27. - 29.5.1975

/16/ R. Suchentrunk
Metal Matrix Composite Materials for Space Application
Metall, 1980 in Preparation

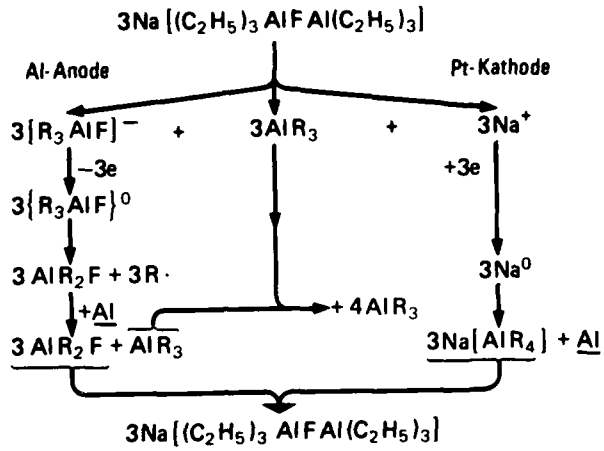


Fig. 1: Electrochemical reactions of aluminium deposition (7)

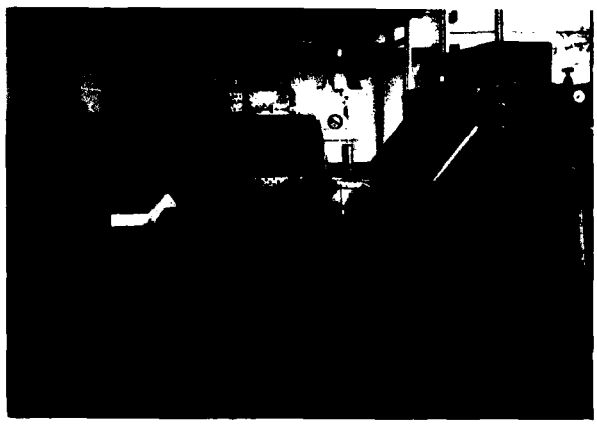

Fig. 2: Aluminium Electro-plating Facility

Fig. 3: Plating Cell

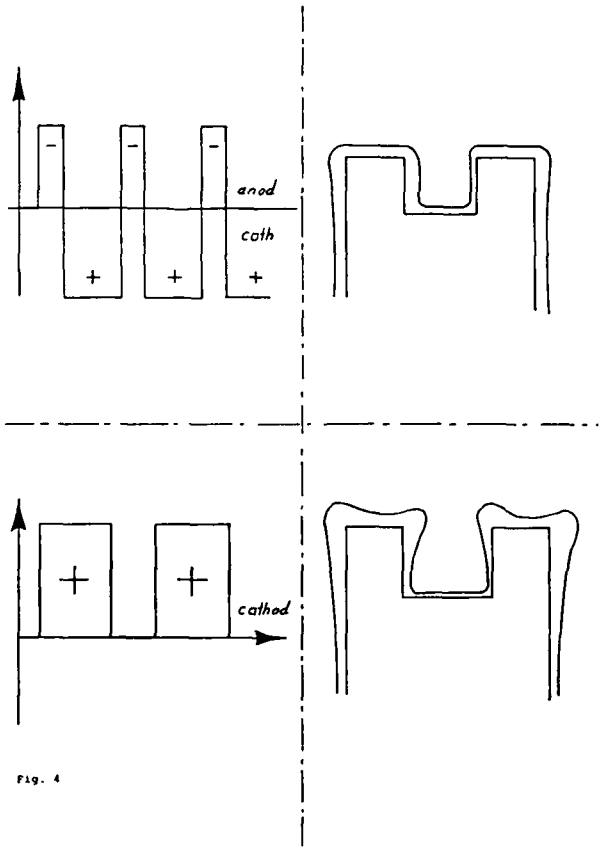


Fig. 4: Thickness distribution by use of various current forms

Fig. 5: micrograph of aluminium coated 1.7734 steel after salt-spray test (magnification 1:200)

Fig. 6: micrograph of ceramically coated Ultrafort 301 steel after salt-spray test (1:200)

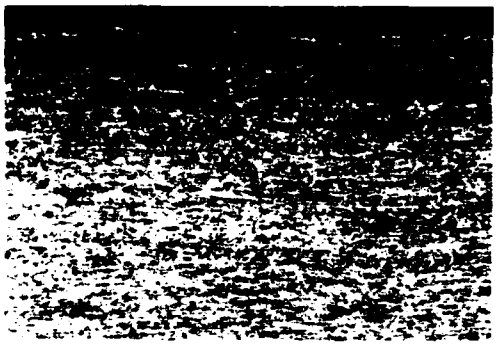

Fig. 7: micrograph of 1.7734 steel coated with organic resin after salt-spray test

Fig. 8: micrograph of aluminium-coated fastener (magnification 1:30)

Fig. 9: micrograph of aluminium coated fastener (magnification 1:30)

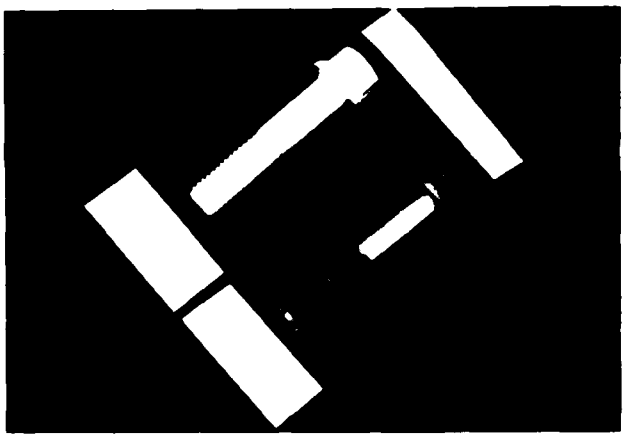

Fig. 10: Fasteners before salt-spray testing

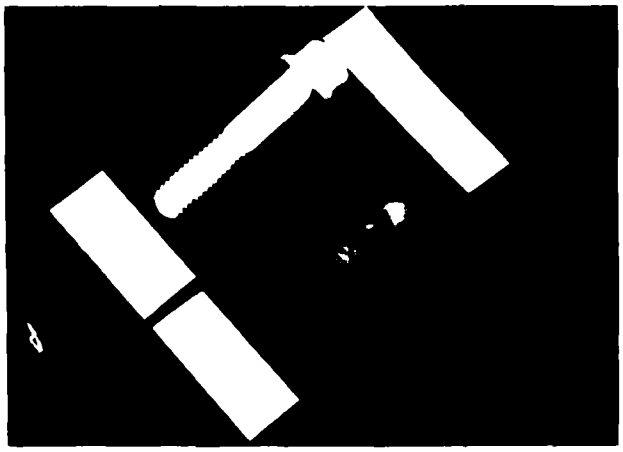

Fig. 11: Fastener after salt-spray testing

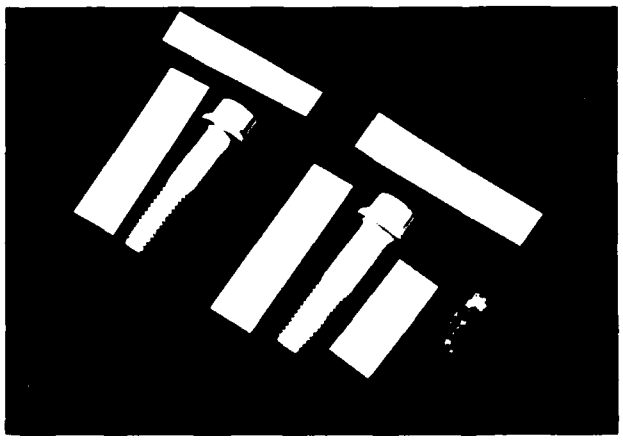

Fig. 12: aluminium-coated fasteners, chromate-treated and uncoated (salt-spray test)

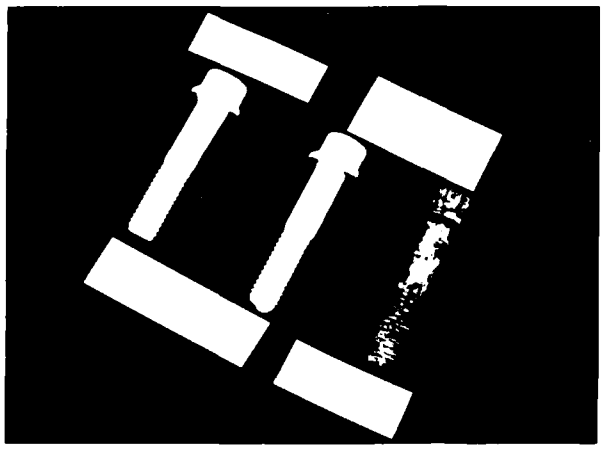

Fig. 13: aluminum-coated fasteners, dc-sulfuric acid anodized and [illegible]-coated - humidity [illegible]

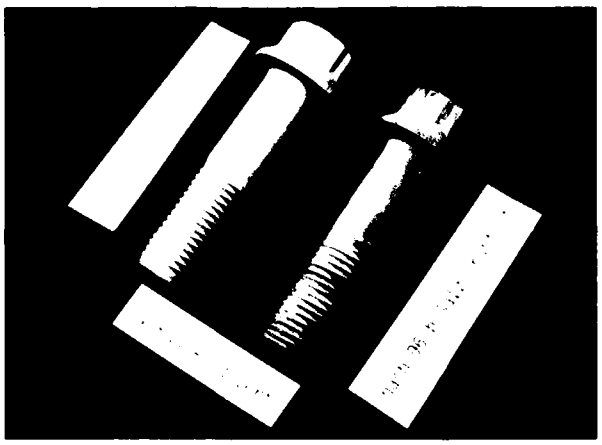

Fig. 14: cadmium-coated fasteners - salt-spray test

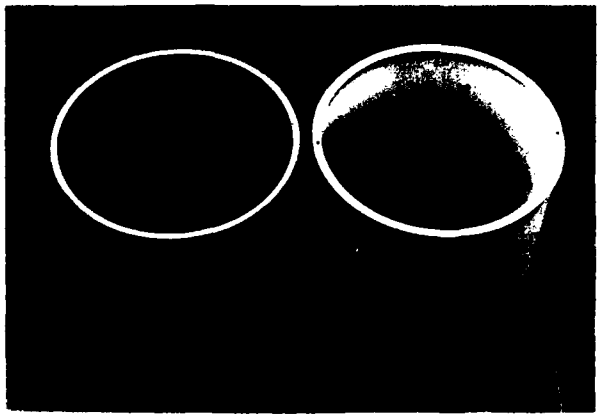

Fig. 15: chromate-treated (left) and dc-sulfuric acid anodized 1.7734 steel tubes (right, after salt-spray test)


Fig. 16: (from left to right): aluminium-coated fasteners,
contact-corrosion tests
al-coated fasteners, salt-spray test
al-coated fasteners, anodized-
chromate treated

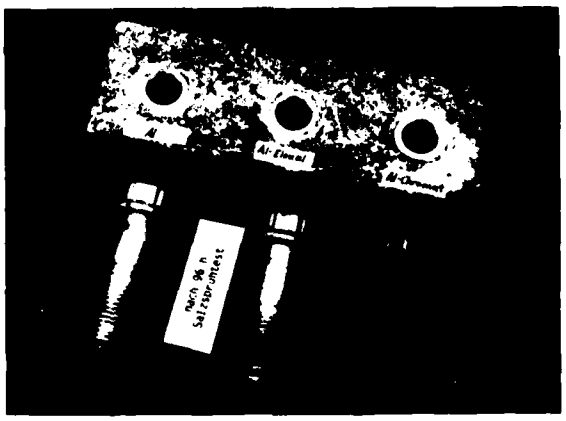


Fig. 17: (from left to right): aluminium-coated fasteners,
contact-corrosion tests
al-coated fasteners, salt-spray test
al-coated fasteners, anodized-
chromate treated


Fig. 18: contact-corrosion tests - humidity
left: cadmium-coated fasteners
right: uncoated fasteners

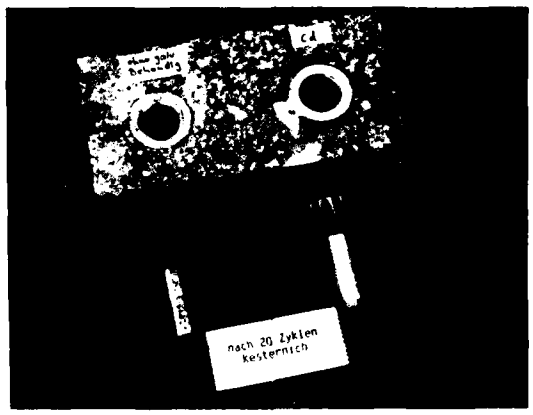


Fig. 19: contact-corrosion tests - humidity
left: cadmium-coated fasteners
right: uncoated fasteners

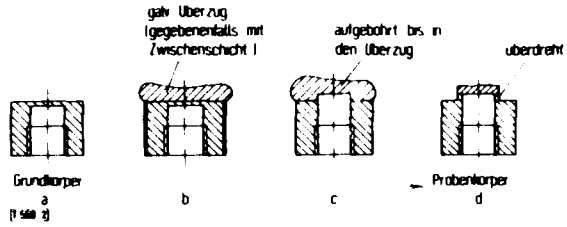


Fig.20: Testing method for the adhesion of metallic deposits (12)

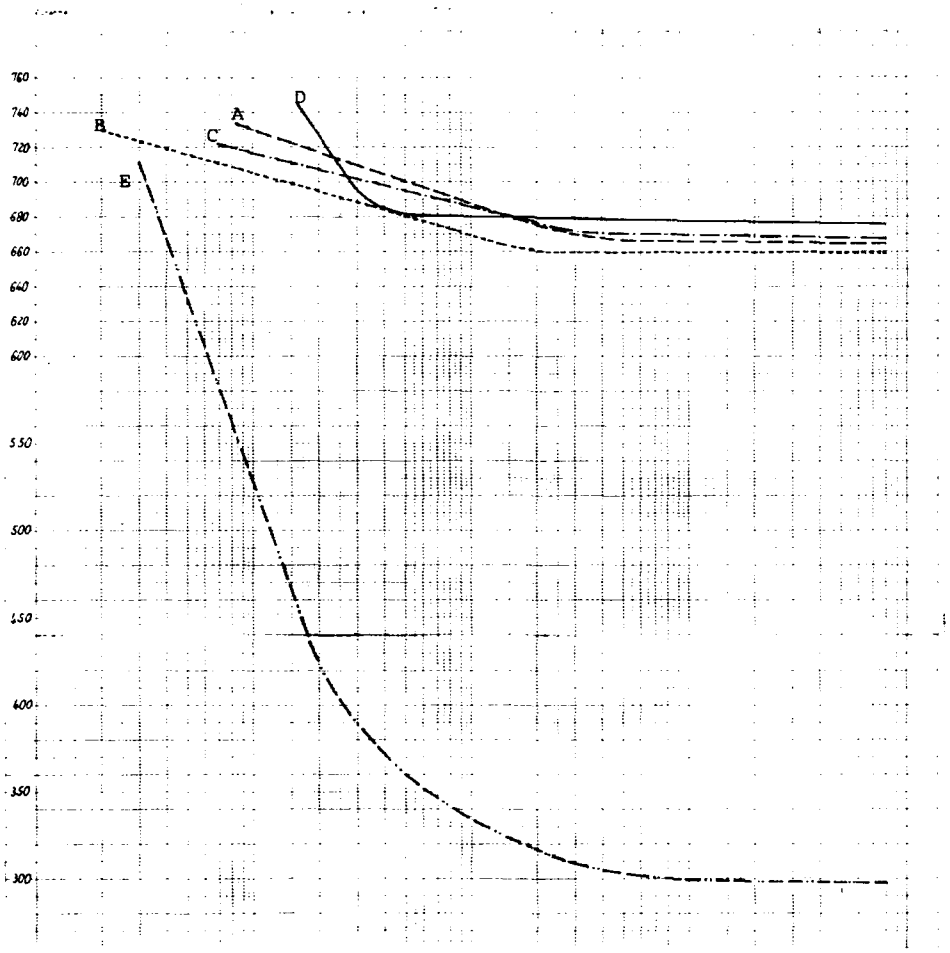


Fig. 21: Fatigue curves of coated steel 1.7734.6 (see 3.4.1)

# OVERLAY COATINGS FOR GAS TURBINE AIRFOILS

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## SUMMARY

The present understanding of the degradation modes associated with gas turbine operation under a variety of conditions is reviewed as a preliminary to defining the needs of protective airfoil coatings and processing techniques. These requirements and present coating procedures are briefly described as an introduction to the need for overlay type coatings in general and electron beam (EB) evaporation processed coatings in particular. A discussion of the features of production EB coaters is followed by a detailed description of the individual coating processing steps involved. While most are identical to other coating procedures, a few are significantly different and are discussed in detail. A review of the understanding of current overlay coating compositions and their use-experience is followed by a brief discussion of future directions in overlay coating processing and composition including electron beam-physical vapor deposition (EB-PVD) applied ceramics.

## INTRODUCTION

It is very important in any discussion of the technology of the application of protective coatings to gas turbine airfoils to have some understanding of the requirements, both of the coated components and of the compositions and processes necessary to withstand these conditions.

Turbine airfoils are one of the most difficult and demanding engineering design and materials challenges today. While their function is rather simple, that of changing air flow direction (vanes) and converting pressure differences into rotary motions (blades), the environment in which they operate is such that they are often the life limiting components of the turbine. As a result, major research efforts are expended in developing new turbine materials, coatings and processes, both to extend the useful lifetime of existing components and to improve their capabilities to allow use under even more severe conditions. It is important to note here, that an airfoil is an elegant combination of a design, a substrate material, its manufacturing process, a coating and its application procedure. It is an engineering system and as a result, in the specification of a protective coating, the selection and use of an application process and the allowable rework procedures are intimately tied into the overall turbine design philosophy.

Airfoils come in a large range of sizes and shapes depending upon the usage requirements for the turbine, its power level and mode of operation. They are produced from a variety of materials by a number of sophisticated manufacturing processes. Some typical airfoils requiring protective coatings are shown in Figure (1). Airfoil material and manufacturing procedure can influence the selection of the coating type and composition. For example, the cobalt base superalloys, often used for higher temperature and lower stressed components such as vanes, do not contain aluminum as an alloying element and, thus are limited in the aluminide coating thicknesses that can be applied without spallation. Superalloy compositions, carefully tailored to be free from the formation of potentially embrittling phases, such as sigma, can be destabilized by coating interdifussion (1). The use of structural strengtheners such as the submicron oxides in the oxide dispersion strengthened (ODS) alloys and the carbides in some directionally solidified (DS) eutectic alloys can also affect coating selection (2).

The need for the use of protective coatings has been well documented (3). However, it may be instructive prior to the description of an advanced coating system to re-emphasize a few key factors which influence the selection of both coating compositon and process.

As demands for improved gas turbine performance and efficiences continued, substrate alloy research programs resulted in the development of higher strength alloys, and the processes to make them, for use in thinner sections and/or at high temperatures. Almost invariably this was at the expense of inherent alloy oxidation/hot corrosion resistance and later on, even coatability. The result often was the use of a new alloy with lower surface stability as a direct replacement with some loss of durability. However, because of the higher strength of the alloy, it was inevitably used at a higher temperature with an even greater sacrifice in uncoated lifetime. In the 1960's protective coatings (in general the aluminides) were used to extend the lifetimes of uncoated airfoils from, for example, 8,000 hours to 12,000 hours, while in the 1970's protective coatings (in general the MCrAlY overlays) were necessary to meet even minimum engine testing and performance demonstration requirements.

The protection of gas turbine systems at high temperatures is effected in the same manner as the protection of other alloys in other corrosion environments. Namely, a stable protective (passive) film, invariably an oxide, is induced to form on the surface of the component. The stability of a number of typical oxide films is shown in Figure (2). The advantages of $Cr_2O_3$ over NiO or CoO are obvious and could be predicted by the success of the many $Cr_2O_3$ forming systems in use today. A problem with $Cr_2O_3$ not shown in this data is the volatility of $CrO_3$ at temperatures above ~ 1,000°C in rapidly flowing air such as

turbine combustion gases (4). Based on these findings, it is not surprising that most gas turbine airfoil coating systems depend upon the formation of an $Al_2O_3$ layer or $Cr_2O_3$ if used at lower temperatures (for severe low temperature hot corrosion with vanadium and other 'bad' fuels, renewed interest has been centered on $SiO_2$ or mixed oxide systems forming $SiO_2$ as one component).

The basis for modern coating technology is the enrichment of an alloy surface layer by a diffusion or overlay process such that, in service, a suitable protective oxide layer will be formed. Thus, this 'coating' does not furnish the direct protection, but provides for the formation of the protective oxide layer. Degradation of these systems usually involves the cyclic loss of this layer by thermally induced spallation and its subsequent reformation. At some point in service lifetime, an insufficient amount (activity) of the critical element, e.g., aluminum, is available for the desired oxide to form and a less protective layer, incorporating critical substrate alloying materials is formed. Rapid weight loss, substrate attack and mechanical property degradation occur at this point and component removal must be promptly initiated if refurbishment is desired.

In the presence of air and/or fuel derived contaminants such as sea salt and heavy metals, molten turbine deposits can occur which greatly accelerate the oxidation degradation process (5). Often the effect of these deposits is to interfere with the protective oxide layer, either its formation or stability. Most present theories attribute the attack to fluxing of the protective oxide, and the accelerated degradation is referred to as 'hot' corrosion. Because of the necessity for the presence of a molten flux (often a mixture based on $Na_2SO_4$) the attack can be more aggressive at the low to intermediate temperatures (600 - 850°C). The presence of erosive particles in the gas stream can also serve to increase the rate of removal of the oxide particularly in the presence of a corrodant. This is thought to be primarily a problem with land based turbines and with the use of low grade fuels.

In recent years, the careful documentation of the various service coating degradation morphologies has greatly aided in the understanding of the attack mechanisms and in the identification and development of appropriate protective coating systems (5).

One additional potential coating related mode of failure should also be mentioned: mechanical degradation, such as thermal fatigue and creep rupture. With today's structurally complex susbstrate alloys, the presence of a coating and the effects of the coating application process on the substrate must be considered in the development and specification of a coating system. In addition to the compositional and processing effects of the presence of a coating, the physical effects (the behavior of the systems as a composite structure) are only recently being given proper attention in the literature (6).

## PROTECTIVE COATINGS

As can be seen from the other papers of this symposium, a variety of techniques are presently available for the application of coatings and it is not surprising, considering the importance of the problem, that many, if not all, are being used or have been considered for the protection of materials in the gas turbine. As detailed elsewhere (3, 4) present day coating techniques can be divided into essentially three types as shown in Table (I). We will briefly review some of the salient features, advantages, and limitations of these various coatings.

The most widely used coating system for turbine airfoils is the chemical vapor deposition (CVD) aluminizing process, either in the pack (pack aluminizing) or out of the pack. It was introduced in the late 1950s as the use temperature and strength requirements of the second generation gas turbines necessitated the selection of lower chromium level superalloys. At these increased temperatures, even the existing alloys were incapable of providing the necessary durability and lifetimes.

The aluminizing process and the resulting structures are now well understood and explanable (7). It is important to note that this in-depth understanding is probably one reason for the widespread and successful use of these coatings and an equivalent level of understanding is necessary in the other coating technologies for their optimum utilization.

The structure of a typical three zone high activity (inward type) aluminide coating on a nickel base superalloy is shown in Figure (3) together with a list of some of its features and limitations. Because the coating depends upon the substrate for all elements but the aluminum, the composition and hence, properties of the coating depend, to a large extent, upon the particular alloy used. As the substrate alloys have been strengthened, they contain less chromium, more carbide phases and second phase reinforcement such as TaC or oxide dispersions, the quality of the coatings and their protectivity have decreased. Therefore, it is not surprising that the aluminides were not able to provide the required protectivity for advanced gas trubines being produced in the late 1960s, or many commercial, marine and industrial turbines being produced in the 1970s. In addition to the limitation of inadequate protectivity, another problem with the aluminides arose with the use of thin walls and air cooling. High surface tensile strains produced by rapid cooling and cooling hole stress raisers resulted in thermal fatigue cracking of these coatings. The NiAl, CoAl type aluminides have a high brittle-to-ductile transition temperature with corresponding low ductilities, less than 0.5 per cent at the temperatures where maximum tensile stresses can occur (8). Premature cracking of critical airfoils can result. Attempts to lower the transition temperature by the reduction in coating aluminum content are limited by diffusional considerations and the required coating lifetime

In the mid-1960s the ability to produce a coating tailored for the specific environmental and mechanical conditions, independent of the susbstrate composition and structure, was required. Attempts to modify the composition of the aluminide coatings by means of pre-surface treatment such as chromizing or noble metal plating have been partially successful for certain applications. However, because of limitations such as the solubility of chromium in the NiAl phase, the effect of a prior chromizing treatment on substrate stability and the limited ductility of the NiAl and noble metal intermetallic phase, for many applications, a more ductile and totally substrate independent coating was still required. Such coatings have been termed an overlay type and depend completely for their composition on the deposition process as opposed to the previously discussed diffusion type coatings. Figure (4) shows the microstructure of an EB-PVD applied CoCrAlY overlay coating that will be discussed below. For the deposition of protective overlay coating compositions a number of application techniques are possible as listed in Table (II).

During the development of overlay composition and processes in the 1960s the electron beam evaporation physical vapor deposition process emerged as the most suitable, and a strong production technology has developed over the past ten years. These developments resulted from the joint efforts of Pratt & Whitney Aircraft, East Hartford, Connecticut and Airco Temescal in Berkeley, California. Recent increases in the use of overlay coatings for the expanding number of commercial and military aircraft gas turbine engines as well as marine and land base propulsion and power generating turbines has accelerated the interest in overlay composition and processing techniques particularly sputtering and plasma spray. However, the EB-PVD process is presently the primary production technique and will be the basis for the following discussion.

## THE OVERLAY COATER

At present there are at least two suppliers of production EB-PVD airfoil coaters and while there are some significant design differences between them (which are not covered in this paper) the basic functions are essentially the same. Figure (5) is a schematic drawing of a multi load lock coater showing the basic components and features.

Like the gas turbine engine, the EB-PVD coater is simple in theory, but more complex in actual operation. In a suitable vacuum environment, generally $10^{-4}$ to $10^{-6}$ torr an electron beam is impinged on a water-cooled copper hearth containing the material to be evaporated. A continuous ingot feeding system is used to maintain the molten pool height and composition at an equilibrium condition. Evaporation rate and coating thickness build-up are often monitored and controlled by a laser pool height indicator with suitable feedback to an ingot feed system. The shape and size of the ingot can vary, but is dictated primarily by present vacuum induction melting capabilities and the properties of these relatively high aluminum content coating alloys. They usually consist of 5 to 10 cm diameter bar stock.

Due to the shape and distribution of the elements in the vapor cloud, the ingot composition can be different from the specified airfoil composition (9). In addition, the composition of the molten pool is different from both. However, under equilibrium conditions, which are rapidly established at pool temperatures of 1,600 - 1,900°C, the composition of the vapor out of the pool must be equal to the composition of the ingot being fed into the pool. The size and the shape of the crucible is selected to maximize deposition and thermal efficiency and, in many coaters, the shape and density of the electron beam is controlled, producing a specific pool temperature profile with corresponding vapor composition and density distribution (10).

The EB power requirements vary with the coater size, the number of airfoils that can be properly positioned in the vapor cloud and the desired rate of coating deposition. Presently, coater power supplies are in the 100 - 200 KW range. While, early studies for other PVD systems indicated that increasing evaporation rates (which are proportional to deposition rates) resulted in a reduced quality coating structure, recent studies on MCrAlY airfoil coatings revealed the opposite. The quality of the deposited coating increased as the evaporation/deposition rate was increasded (11). Deposition rates exceeding 25 μm/min are common as opposed to high rate sputtering techniques were 25 μm/hour are still being sought (12). The effect of these high deposition rates coupled with advanced part handling and tooling, discussed below, is coater throughput exceeding 500 standard size parts in an eight hour shift.

The results of these and other process and equipment improvements over the past ten years has been the reduction in the coating price for a typical size airfoil, e.g., JT9D first blade. It has been estimated that the price for a fully processed component in quantities of 5 - 10,000 per month has decreased from ~ $85 in the early 1970s to ~ $40 in 1980 (13). Other coater features such as preheating and oversource heating capabilities follow good vacuum furnace design criteria and will be discussed below, where appropriate, in conjunction with processing details.

## THE OVERLAY COATING PROCESS

Although in this paper and elsewhere most of the attention is directed towards the actual deposition of the overlay coating on an airfoil, a significant part of the process, time, expense and manpower can occur during the pre- and post-coating processing steps. A typical list of the processing sequence is shown in Table (III). As is inferred, the actual coating deposition steps can be as little as 40 - 50 per cent of the total 'coating' cycle. Many of the individual steps are straight forward and are common to most other

coating procedures discussed in this lecture series and elsewhere and need only be listed. Examples include inspection, post coating heat treatment and shipping. However, certain steps are critical and unique to the PVD process and will be described in more detail below.

Surface Preparation. Surface cleaning operations provide the standard function of removing scale, oxides and dirt from previous operations and can vary with the history of the part and substrate alloy. In general, however, they involve an abrasive blast or tumbling operation(s) followed by suitable cleaning to remove embedded grit. But, unlike some coating techniques, production of a given level of surface roughness, often greater than 100 μ in, is not required for adherence and, in fact, may be detrimental in its effect upon columnar coating growth as discussed below.

Coating Masking. Because the EB-PVD coating process is essentially line-of-sight, procedures necessary to protect 'no-coat' areas on specification drawings can be relatively simple. However, it must be remembered that the masked part can undergo a thermal cycle to ~ 1,000°C for periods of 5 - 30 min. Masking is often best accomplished by proper part holder design and final machining sequencing. Additional masking can be required for areas such as blade tip shrouds and for this purpose mechanical and/or chemical barriers are used. As in the pack cementation process, specific systems used are often proprietary and represent a compromise between ease of the application, effectiveness, attack of substrate and ease of removal.

Pre-Coater Processing. In the coating process, properly prepared airfoils are loaded into tooling which serve the dual function of holding and maneuvering the part in the vapor cloud and masking or shielding specified coating-free areas from the essentially line-of-sight vapor. In most instances, the tooling design and construction is proprietary and unique for specific airfoil shape and coating requirements. Recently disclosed patents detail a modified planetary system which allows multiple parts to be supported from one shaft, independently rotated and indexed in the coating vapor to obtain the required thickness profile (14/15) The use of such multiple part tooling together with multiple shaft coaters and increased evaporation rates has increased coater throughput from less than 100 to over 500 parts per shift.

Coating Deposition. The PVD coating of airfoils differs in two significant ways from other coating processes and techniques. First, the substrate to be coated is preheated in vacuum ~ 1,000°C prior to exposure to the coating vapor (16). During coating deposition, the substrate is maintained at temperture by a combination of pool radiation, heat of condensation and an additional over source heater. The use of pre-heating and a heated substrate during coating results in the deposition of an adherent coating with some minimal amount of substrate-coating interdiffusion occuring during the coating cycle. Coating spallation, a problem with many coating processes and systems, is, thus, not a problem for properly cleaned substrates. In some EB-PVD coating work, where argon gas is used to promote randomnization of the essentially line-of-sight evaporation, sufficient cooling of the vapor can occur with the result that decreased structural quality and poor adherence is seen. For these conditions the use of a substrate bias, so-called ion-plating can be used to provide the additional energy necessary for the required surface atom mobility and interdiffusion (17). The optimum temperature depends upon the system involved and can range from 800 - 1,100°C. A finer as-deposited structure results at the lower deposition temperature and a coarse grain structure and more substrate interdiffusion at the higher temperatures. In addition, some surface re-evaporation can occur at the higher temperatures. For the deposition of MCrAlYs on typical superalloy substrates, 1,000°C is often found to be a convenient temperature and is compatible with most alloy heat treatments as well.

A second feature of the EB-PVD overlay coating process is the rotation of the substrate during deposition. Coatings deposited on a rotated substrate often have an as-deposited columnar grain structure with unbonded interfaces known as 'leaders'. These structures have been shown to result from the shadowing by the individual coatings growing in a preferred direction (18/19). Increasing deposition temperature which increases surface diffusivity reduces the density of these leaders, as does increasing the angle between the surface to be coated and the vapor flux (12).

Post-Coating Processing - Peening. It has been shown that a post-coating surface peening process (often using ~ 200 μm glass beads) followed by a heat treatment results in a complete closure of these leaders and most EB-PVD applied coatings operations including a peening operation. It could be noted that this peening operation also serves to remove chemical masking materials and to clean up areas of coating overspray. Peening has little affect on as-deposited surface smoothness, possibly some slight improvement to ~ 40-60 μ in. Final coated airfoil surface smoothness is an important factor in turbine efficiency and could involve additional processing steps if as-deposited coatings were too rough, e.g., > ~ 100 μ in.

Recoating. As for other coatings a procedure is nessary to allow removal of the overlay coating once applied. This need can result from the generally 1 - 5 per cent coating rejects identified during inspection or from service operated parts. For service parts, because of the expense of complex airfoils, it is desirable to remove the component prior to extensive attack of the substrates. The typical procedure involves stripping the coating, reworking the component and then recoating and subsequent return to service. Presently, a considerable research and development effort is being expended in studying airfoil repair and refurbishmnet techniques including effects of welding, hot isostatic pressing and reheat treatment. This effort and the use of reworked parts is predicted to expand rapidly.

Current EB-PVD coating removal techniques require acid dissolution of the compositionally different coating alloy from the substrate. For many overlay coatings the techniques are similar if not identical to those used for the aluminide coating. Again, some proprietary processes and techniques prevail. One difference between the aluminide and the overlay coating is that since the aluminide involves the interaction with the substrate for its formation, stripping involves the removal of this substrate and greater dimensional changes.

As the compositions of the overlays approach that of the substrate, in particular for aluminum, and/or the substrate because more structurally complex and less corrosion resistant, some problems of removal of the coating without selective attack of the substrate can be expected and techniques such as substrate masking have to be employed. In general, the processing procedures for the EB-PVD applied coatings are little different from other coating procedures. The development of an understanding of metallurgical features of these coatings has allowed a relatively simple transition from the research laboratory to the production floor.

## THE OVERLAY COATINGS - MCrAlY'S

Following the discussions of the techniques and procedures employed in the EB-PVD overlay coating of airfoils, it may be of interest to review the availability and selection of overlay compositions.

At present, a discussion of these compositions is a discussion of the MCrAlY (M = Fe, Co and/or Ni) coatings (3). Early interest focused on several cobalt base CoCrAlYs of relatively similar Cr, Al and Y levels and these have been the primary compositions used in production. The reasons for the selection of a specific composition has been discussed in the literature in some detail and involves many considerations and trade-offs as occur in any materials selection procedure for a critical component such as a turbine airfoil. However, increasing demand as previously noted has resulted in the need to develop additional compositions for more specific applications such as extended operation in a marine environment or high temperature operation with high thermal fatigue strains on controlled solidification alloys in advanced military environments. Improvements in the process have also resulted in a decrease in the compositional range that can be specified and controlled. The result is that where one or two compositions were in use ten years ago, today, over thirty production and experimental compositions are in use or under active developmnet. It should be cautioned that, as yet, many of these specific coatings are proprietary.

Some factors involved in the selection and level of the MCrAlY are elements and are briefly reviewed below.

Chromium is present primarily to provide oxidation and hot corrosion resistance of the coating. Because of the potential scarcity and cost, the trend is to use these critical elements in the small volume coating and not the larger volume substrate. Also, the detrimental effects of higher chromium levels on mechanical properties of superalloys are not a concern in the essentially non-load carrying coatings. However, the use of too high a level in the coating could affect substrate stability. The presence of chromium has the effect of increasing the aluminum activity of these coatings such that protective $Al_2O_3$ can be formed to lower aluminum levels. This allows the use of compositions with lower aluminum contents and hence improved mechanical properties.

Auminum is present to form $Al_2O_3$ as previously discussed. While, higher levels result in longer lifetimes (at least under oxidizing conditions) excessive brittleness and a higher temperature ductile-brittle transition temperature can result. The trend is to use aluminum levels below 12 per cent and coatings in the 5 - 10 per cent range are presently being explored.

The key to success of most overlay coating compositions is the presence (and possibly location) of an oxygen active element such as yttrium. In a, not completely defined, manner these elements promote adherence of the $Al_2O_3$ layer during extended cyclic exposures, resulting in an increase in coating protectivity at lower aluminum levels. The MCrAlY's with ~ 12 per cent Al are significatnly more protective than the aluminides with ~ 30 per cent Al. The ductilities of the lower aluminum MCrAlY's are also a significant feature of the active elements containing coatings as has been documented.

The continual demand for improvements in overlay coating performance has resulted in a number of active coating development efforts being initiated during the past several years. It is predicted that results of these programs will result in the use of even more complex coating compositions and the introduction of structural as well as compositional control. The latter through the use of second phase particle additions.

## SERVICE EXPERIENCE

EB-PVD coatings have been in service for approximately ten years on JT9D, FT4 and other gas turbines, and their use continues to expand and increase. Because of proprietary positions and for competitive reasons, little specific information on data is available in print, except for the reported increasing overhaul time and performance for turbines using overlay coatings. It was recently reported in Aviation Week (20), that the JT10D would incorporate the most advanced single crystal turbine airfoil and a NiCoCrAlY, EB-PVD overlay coating. Likewise, the newly designed F-100 first turbine blade produced in the Pratt & Whitney Aircraft foundry will use this trend towards advanced alloy and coating technology such as EB-PVD.

## NEW DIRECTIONS IN EB-PVD

Due to these trends towards increased coating complexity, coupled with the concern for the ability of an evaporation type process to produce deposits containing elements with greatly varying vapor pressure, recent studies have been directed towards better defining the capabilities of the EB-PVD process. Although, studies are continuing, it has been shown that five and six element MCrAlY coating compositions containing elements with varying vapor pressures could be produced (21), e.g. CoCrAl coating containing the active element addition, hafnium, or hafnium and yttrium was deposited using a production coater. There has been considerable interest in the potential benefical effects of hafnium coating additions. In addition, with the use of a multi source evaporation unit, a coating with composition graded from the substrate to the surface can be produced as well as a two phase structure containing some oxide dispersion.

Further investigation has shown that ceramics as well as metallic coating compositions can be deposited using the EB-PVD process (22). For example, coatings varying in thickness from 25 μm to 250 μm have been deposited with stabilized cubic zirconia structures and growth morphologies portending improved thermal fatigue resistance. The use of a ceramic coating on a metal substrate offers the tantalizing combination of the ceramics surface stability and thermal barrier properties on a tough, high strength superalloy substrate. In the case of ceramic coatings, the control of the structure is found to be possibly as important as the composition itself in promoting resistance to thermal fatigue induced spallation. Activity in this area of ceramic thermal barrier coatings is predicted to increase as rig and engine testing continues to report favorable results.

## REFERENCES


1. G. F. Paskiet, D. H. Boone and C. P. Sullivan, "Effect of Aluminide Coating on the High-Cycle Fatigue Behavior of a Nickel-Base High Temperature Alloy", J. Institute of Metals, 100 (1972) pp. 58-67.

2. T. E. Strangman, E. J. Felten and R. S. Benden, NASA, "Refinement of Promising Coating Compositions for Directionally Cast Eutectics", 1976, Report No. CR 135103.

3. G. W. Goward, "Protective Coatings for High Temperature Alloys", State of Technology, proceedings of symposium on High Temperature Alloys - Electrochemical Society, Las Vegas, October 17-22, 1976.

4. G. W. Goward, "Current Reseach on the Surface Protection of Superalloys for Gas Turbine Engines", J. Metals, 22, October 10, 1970, p.31.

5. F. S. Pettit et al, "Oxidation and Hot Corrosion Resistance", Chapter X, Alloy and Microstructural Design, Edited by J. K. Tien and G. S. Ansell, Academic Press, 1976.

6. T. E. Strangman and D. H. Boone, "Composition and Processing Considerations for the Mechanical Behavior of Coating-Superalloy Systems", presented at 4th Conference on the Behavior of Materials in Marine Environments, 25-28 June, 1979 (published in the proceedings).

7. G. W. Goward and D. H. Boone, "Mechanisms of Formation of Diffusion Aluminide Coatings on Nickel-Base Superalloys", Oxidation of Metals, 3, p.475, 1971.

8. D. H. Boone and G. W. Goward, "The Use of Nickel-Aluminum Intermetallic Systems as Coatings for High Temperature Nickel Base Alloys", proceedings of 3rd Bolton Landing Conference, Claitor's Publishing Division, Baton Rouge, 1970, p.545.

9. R. C. Krutenat, Gas Turbine Materials Conference Proceedings, NAVSEA/NAVAIR, 1972, p.136.

10. D. H. Boone and E. D. Erikson, "Advances in EB Overlay Coating Technology and Processing Capabilities", proceedings 3rd Conference on Gas Turbine Materials in a Marine Environment, Bath, U.K., September 1976.

11. D. H. Boone, S. Shen and D. Lee, "Effect of Deposition Rates on Overlay Coating Structure", presented at the International Conference on Metallurgical Coatings, San Francisco, April, 1978.

12. R. J. Hecht, Pratt & Whitney Aircraft Group, "Scale-Up of Advanced MCrAlY Coating Process", 1979, Report No. FR 12170.

13. L. M. Bianchi and S. Shen, "Electron Beam Overlay Coatings Grow Worldwide", presented at 6th International Conference on Metallurgical Coatings, San Diego, April 1979 (to be published in the proceedings in Thin Solid Films).

14. G. R. Scheuermann, "Rotatable Substrate Holder For Use In Vacuum", U.S. Patent #4,108,107, August 22, 1978 (assigned to Airco Temescal).

15. G. R. Scheuermann, "Orbiting and Rotating Substrate", U.S. Patent #4,122,221, October 24, 1978 (assigned to Airco Temescal).

16. K. D. Kennedy, "Vapor Deposition Method Including Specified Solid Angle of Radiant Heater", U.S. Patent #3,560,252, February 2, 1971 (assigned to Airco Temescal).

17. D. H. Boone, D. Lee and J. M. Shafer, "The Electron Beam Coating of Turbine Components and Ion Plating", Conference Ion Plating & Allied Techniques, IPAT 77, Edinburgh, June 1977 (published in the proceedings).

18. D. H. Boone, T. E. Strangman and L. W. Wilson, "Some Effects of Structure and Composition on the Properties of Electron Beam Vapor Deposited Coatings for Gas Turbine Superalloys", J. Vacuum Science and Technology, 11, 1974, pp.641 to 646.

19. W. Grossklau, N. E. Ulion and H. A. Beale, "Some Effects of Structure and Composition on the Properties of Electron Beam Vapor Deposited Coatings for Gas Turbine Superalloys", Part II - The origin of Defect, Thin Solid Films, 40, 1977, p.271

20. "Single Crystal Technology Use Starting", Aviation Week & Space Technology, October 1, 1979, p.69

21. D. H. Boone, S. Shen and R. McKoon, "Electron Beam Evaporation of Low Vapor Pressure Elements in MCrAl Coating Compositions", presented at 6th International Conference on Metallurgical Coatings, April 1979, San Diego, published in the proceedings in Thin Solid Films (in press).

22. D. H. Boone, S. Shen and J. W. Fairbanks, "Advanced Gas Turbine Coatings for Minimally Processed Coal Derived Liquid Fuels", presented at the Conference on Advanced Materials for Alternate Fuel Capable Directly Heat Engines, July 1979, Castine, Maine, published in the proceedings.

## TABLE 1

## POTENTIAL GAS TURBINE AIRFOIL COATING TYPES

DIFFUSION COATINGS:-

ALUMINUM, THE ALUMINIDES
CHROMIUM, CHROMIZING TREATMENTS
SILICON, THE SILICIDES

DUPLEX COATINGS:-

A LAYER PLUS A DIFFUSION COATING,
E.G., A NOBLE METAL LAYER PLUS
ALUMINIZING OR CHROMIZING PLUS
ALUMINIZING

OVERLAY COATINGS:-

COATING COMPOSITION INDEPENDENT OF
SUBSTRATE

## Table II

## Potential Protective Overlay Coating Application Processes

PHYSICAL VAPOR DEPOSITION

A) ELECTRON BEAM EVAPORATION AND VARIATIONS SUCH AS ION PLATING
B) SPUTTERING

THERMAL SPRAYING

A) PLASMA
B) SHIELDED PLASMA
C) LOW PRESSURE PLASMA

CHEMICAL VAPOR DEPOSITION

FUSED SALT ELECTROLYSIS

LASER FUSION

## Table III

## List Of EB-PVD Processing Steps

Receiving

Inspection and Batching

Surface Preparation:-
- Degreasing
- Grit Blasting
- Vapor Honing

Weighing
(if used as thickness and process control)

Loading Into Fixtures and Masking

Coating Cycle
- Pre-heat
- Coating Deposition
- Cooling

Remove From Fixtures

Weighing

Overspray Removal

Peening

Diffusion Heat-Treatment
(often substrate alloy solution treatment)

Aging Heat-Treatment
(if specified)

Inspection and Documentation

Shipment

Reworking - if applicable
(stripping and re-cycling through appropriate process)

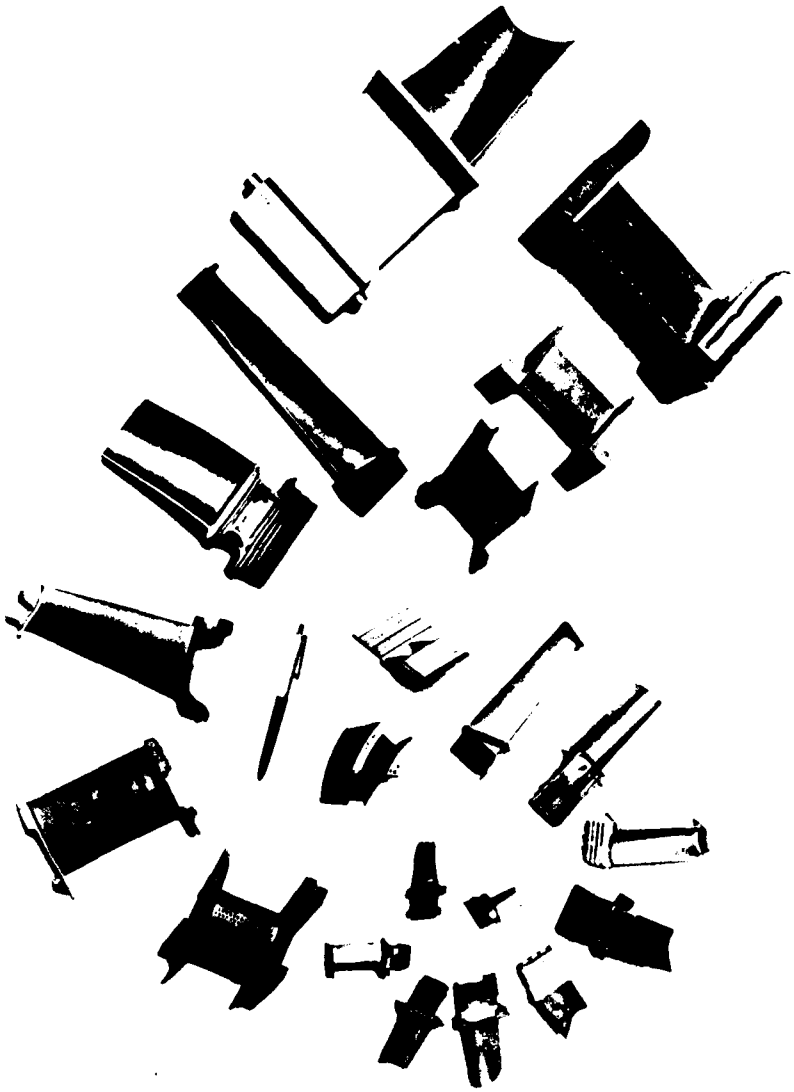


FIG. 1. TYPICAL GAS TURBINE AIRFOIL GEOMETRIES THAT REQUIRE PROTECTIVE COATING SHOWING REQUIREMENTS FOR ADVANCED COATING PROCESSING TECHNIQUES

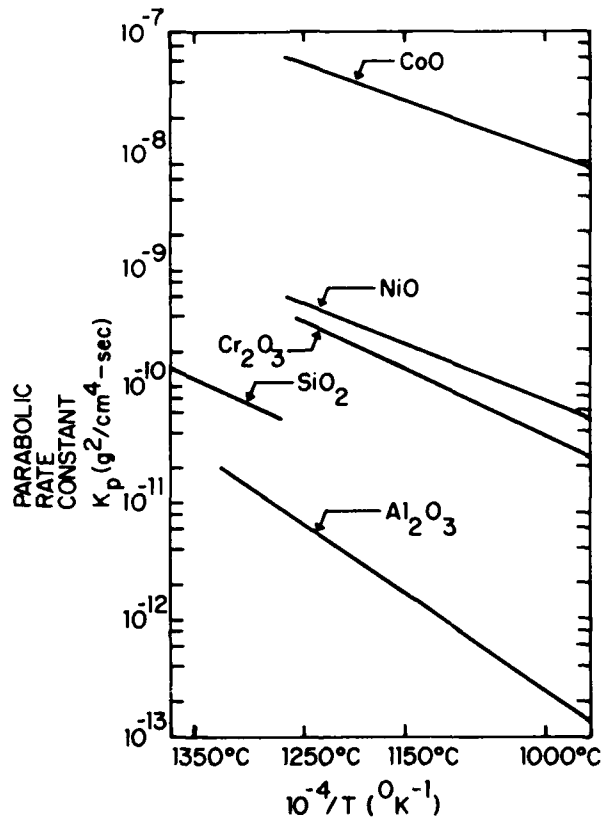
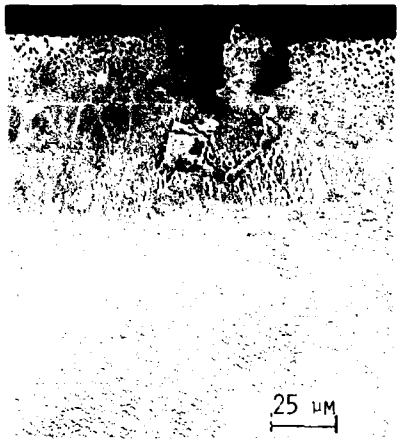



FIG. 2. PLOT OF PARABOLIC RATE CONSTANT VERSUS $^1/T$ FOR VARIOUS METALS FORMING CoO, NiO, $Cr_2O_3$, $SiO_2$ AND $AL_2O_3$ LAYERS SHOWING THE DIFFUSIONAL STABILITY OF $AL_2O_3$ FORMING SYSTEM (5).

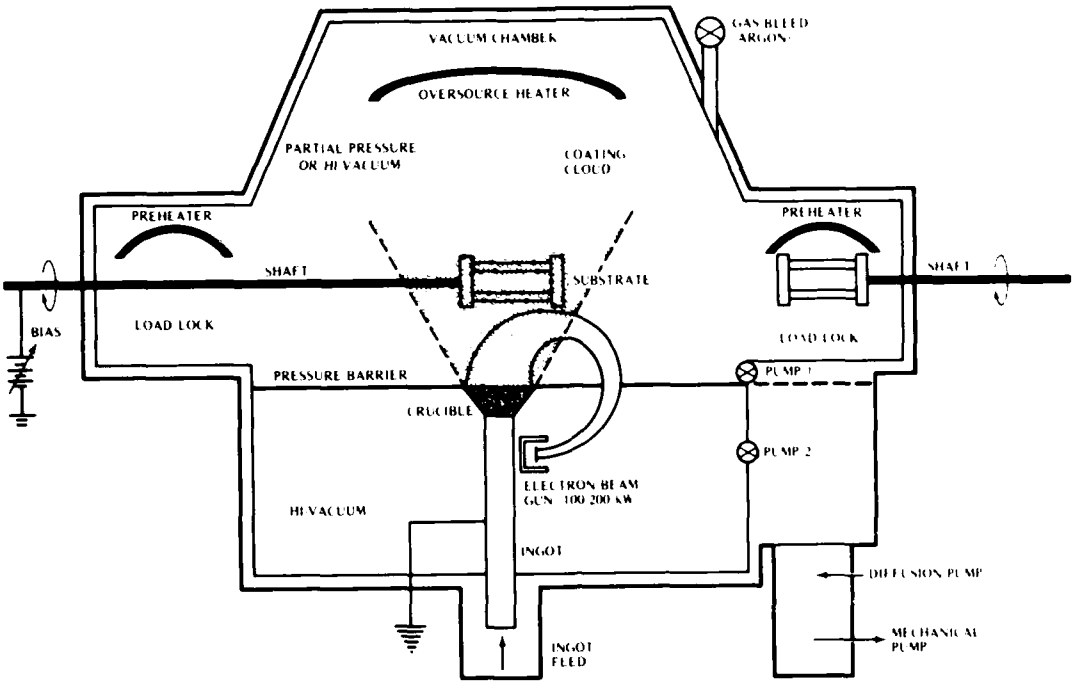
## ALUMINIDE COATINGS




| ADVANTAGES | LIMITATIONS |
|---|---|
| SIMPLE PROCESS | SUBSTRATE COMPOSITION AND PROCESS LIMITED |
| INEXPENSIVE | SUBSTRATE STRUCTURE LIMITED |
| NON LINE-OF-SIGHT | LIMITED LOW TEMPERATURE DUCTILITY |
| GOOD OXIDATION RESISTANCE | LIMITED ACTIVE ELEMENT EFFECT |

FIG. 3. MICROSTRUCTURE OF AN INWARD TYPE, THREE ZONE ALUMINIDE COATING ON A NICKEL BASE SUPERALLOY AND ADVANTAGES AND LIMITATIONS OF THE PROCESS. NOTE PREFERENTIAL OXIDATION OF SUBSTRATE CARBIDES ENTRAPPED IN OUTER ZONE.


FIG. 4. MICROSTRUCTURE OF EB-PVD APPLIED CoCrAlY COATING SHOWING MIMIMUM ZONE OF COATING-SUBSTRATE INTERDIFFUSION




SCHEMATIC OF 200 KW COATER WITH GAS SCATTERING AND BIAS CAPABILITIES

FIG. 5. SCHEMATIC REPRESENTATION OF A TWO LOAD LOCK EB-PVD AIRFOIL COATER SHOWING RELATIVE LOCATION OF KEY COMPONENTS AND OPERATIONS. PROVISIONS FOR GAS BLEED AND SUBSTRATE BIASING ARE ALSO SHOWN IF REQUIRED FOR 'ION PLATING'

# APPLICATIONS OF SPRAYED COATINGS

by

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SUMMARY

In modern aircraft a multitude of sprayed coatings for diverse applications are being used. The coating properties must meet the service demands which may be classified as:

- preventing, fretting, wear and corrosion;
- controlled abradability;
- thermal barrier.

Developments in both coating equipment and coating materials have in several instances allowed production of coatings which match the performance demands.

In the paper, some typical applications of sprayed coatings in aircraft-components are discussed.

## 1. INTRODUCTION

During the past fifteen years, sprayed coatings have become an integral part of both the original equipment manufacture and the repair, for instance of gas turbine engine components. Under high temperature cycling, sandwich coatings with graded metal-ceramic composition, provide an effective thermal barrier on the thin-walled components of combustion chambers. Ceramic/metallic thermal barrier coatings are used to reduce metal operating temperatures.

Higher temperatures will be used to increase the power of jet engines. Because the gas turbine engine environment is more hostile than before, improved high temperature coatings are being developed to protect turbine parts against such conditions as oxidation or erosion. At the present, protective hot gas corrosion coatings of the MCrAlY-type are plasma sprayed under low pressure conditions to protect the exposed parts.

Furthermore, current engine design practice dictate that the turbine blade tip clearance to the outer frame seal should be kept to an absolute minimum for maximum efficiency. By means of thermal spraying, this problem can be solved satisfactorily.

Non-lubricated mating parts of mechanical components in aircraft jet engines can be protected from vibration, fretting, impact and hammer wear by application of thermally sprayed coatings. Thus, one of the persistant major problems facing the airline industry can partially be solved.

Besides technological and metallurgical advantages, application of thermal spraying techniques can result in considerable savings as compared with other surface coating technologies. In selecting the suitable spray material, the environmental and mechanical loading conditions have to be taken into account.

## 2. APPLICATION OF WEAR RESISTANT COATINGS

For operating temperatures up to 540° C, tungsten carbide base coatings are most successful for optimum performance under given wear conditions. Thus, they are recommended for compressor, diffuser and accessory section, as well as for select "cool" areas in the combustion and turbine sections. The type of wear and environmental conditions will usually determine the optimum protection system to be specified /1/.

For operating temperatures above 540° C, chromium carbide base coatings in addition to cobalt base coatings have been found to be useful. These materials are used for applications at temperatures in the 540° C to 980° C range /1/.

Powder mixtures of 15 % Ni and 85 % $WTiC_2$, or 25 % NiCr and 75 % $Cr_3C_2$ are also successfully employed at temperatures above 500° C /2/. In the case of the last mentioned powder, a core existing of $Cr_3C_2$ is unveloped by a Ni-Cr layer. Besides the excellent wear resistance during operation at temperatures above 500°C, these coatings provide sufficient resistance against oxidation. The most critical temperature range is between 480° C and 590° C /3/. Neither the tungsten carbide nor chromium carbide base coatings show satisfactory oxidation resistance. The temperature range is too high for tungsten carbide and too low for the regenerative formation of naturally lubricative oxide films on $Cr_3C_2$. Titanium carbide based coatings may fill this gap /3/.

For many years, chromium carbide has been the main sprayed coating system offering wear resistance at temperatures between 550° C and 1000° C. Whilst this coating has given excellent service in many applications, there has been a long standing need for improvements /5/, and other coating materials have been developed with superior service properties. A range of new coating materials is shown in Table 1. It can be seen that these new coatings are cobalt based alloys. The chart contains the chromium carbide/nickel chromium coating at the bottom to compare it with the new coatings. Due to the double heat treatment the new coatings are stress-relieved, densified, and diffusion bonded to the substrate /5/.

As can be seen in Fig. 1, the new high temperature wear resistant coatings provide excellent wear and oxidation resistance compared with the chromium carbide/nickel chromium coating. The coatings are recommended for the following operating temperatures /5/:

- higher than 980° C : LCO-17A
- 870° C - 980° C : LCO-17A or LCO-19A
- 649° C - 970° C : L -103A or LCO-19A
- less than 649° C : L -103A

One of the major areas where these coatings are applied is the contact surface where turbine and fan or compressor blades interlock, Fig. 2. Such interlock areas are usually located in the mid-span shrouds or tip shrouds. Under characteristic engine operation conditions these interlocks experience the full range of wear mechanisms plus high impacting loads during start-up and shut-down /3/. Metal operating temperatures may vary from minus 18° C to plus 870° C or over. Blade materials include titanium base alloys for fan and compressor blades and nickel base superalloys for the high temperature sections of the turbine. Thus, the requirements for interlock applications are most demanding in view of the 12 000 to 30 000 hour life requirements of the turbofan engines /3/.

Detonation gun spray system is used as well to coat such interlock areas. A typical part coated this way is the mid-span of titanium compressor and fan blades as shown in Fig. 3 /4/. As mentioned above, one area of the gas turbine engine which has received attention from the suppliers of coatings for many years is the turbine interlock shroud wear surface /4/. Fig. 4 shows the process of building up a wear-resistant coating onto a turbine blade shroud with the detonation-gun. Such coatings are very well bonded with bond strengths much in excess of 70 N/mm², and withstand high interface loads of sliding and hammering which often have to be encountered on such faces. Furthermore, the coating may be applied to a specific thickness with high degree of accuracy, such that the coating does not need to be finish machined /5/. In Fig. 5 the effect of notch wear is explained.

Outside the jet engine, numerous parts are coated by thermal spraying techniques. In the following, some examples are given to explain the versatility of this technology. Fig. 6 shows a rotor wheel shaft of an auxiliary power unit which rotates at about 40 000 rpm /6/. The bearing seat to which another impeller is press-fitted develops scoring and wear which may propagate rapidly. The seat is machined, grit-blasted, sprayed with molybdenum and ground to the required dimensions.

High-strength steel landing gear components are protected by thermally sprayed coatings, too. The lugs of the main landing gear of the outer cylinder shown in Fig. 7, are coated by plasma spraying with Ni-Al composite powder /6/. Compared with repair by chromium plating, the overall costs have been cut down by about 40 %. Salvaged components have performed satisfactorily for more than three years before coating replacement /6/.

Generally, thermally sprayed coatings sometimes may reduce the fatigue strength of various alloys, particularly titanium (up to 40 %) /5/. Peening of the surface to be coated along with careful application and control of the coating process as well as avoiding extremely stressed or fatigue-critical areas, does allow sprayed coatings to be used with the utmost confidence.

Fig. 8 shows in diagrammatic form the Mc Donald-Douglas DC-9 wing slat track manufactured in titanium /5/. In the upper diagram the slat track is in cruise position. In the lower diagram it may be seen in take-off and landing position with the slat fully extended. In this position wear occurs between the rollers and the track surface.

After extensive and satisfactory fatigue testing by the manufacturing company, sprayed tracks were evaluated for service properties by a big airline. As a result, coated tracks were found to be recommendable due to good performance and low maintenance and replacement costs.

Another example for successful application of sprayed coatings is the link which locks the nose wheel landing gear in the down position /5/. The jaw of the link was originally chromium-plated and after approximately 400 landings, the chromium plating would be worn through and need replacing. After coating with 0.12 mm of tungsten carbide the wear surfaces of the jaw turned out to be fully serviceable after 1700 landings and were

returned for further service /5/.

## 3. GAS PATH SEALS

Gas path sealing is a proven and accepted method of improving gas turbine engine performance and, thereby, reducing fuel consumption /8/. Reduced operating clearances limit the loss of high energy, high pressure gas from the main gas path without extracting useful work from it. Reducing leakage results in increased turbine efficiency: Current estimation for a typical commercial gas turbine engine is that a 0.254 mm reduction in average operating clearance of first stage high pressure turbine blade tip would permit approximately one percent increase in turbine efficiency /8/. Fig. 9 shows the principle of an abradable gas path seal, which performs two primary functions:

1. It permits operation at minimum clearances by reducing the potential of rotor damage during rotor-seal interactions, and
2. it protects critical turbine parts from excessive temperatures by providing a thermal barrier between the hot gas and the turbine static structure /8/.

Seal materials with increased temperature capability will permit reduction in cooling air requirements and result in improved engine efficiency. If the thermal conductivity of the gas path seal is sufficiently low, the supporting structure is thermally protected and requires less cooling. Furthermore, the reduction in cooling air requirements will improve attendant engine efficiency. For extreme high temperatures (up to 1315° C), a plasma sprayed graded layer of yttria stabilized zirconia ($ZrO_2$)-metal (CoCrAlY) as a seal system for gas turbine blade tip applications was developed /8/. Satisfactory abradability and erosion resistance was demonstrated. Encouraging thermal fatigue tolerance was shown.

## 4. THERMAL BARRIER COATINGS

Ceramic thermal barrier coatings on hot engine parts have the potential to reduce metal temperatures, coolant requirements, costs and complexity of the cooling configuration, and are able to increase life, turbine efficiency and gas temperature /9/.

Thermal barrier systems may be divided into two groups: thick systems, in the order of 0.25 to 0.5 mm, developed for turbine seals - see chapter 3 - and thin systems, less than 0.25 mm, used or developed for airfoils, combustors and similar applications. In this chapter, the thin systems will be considered only.

Generally, thermal barrier coatings are either two layer (duplex) coating systems consisting of a metallic undercoat and a pure oxide overcoat, or multi-layer or continuously graded coatings. The second type of a coating begins with a metallic layer, then has a zone of mixed metal and oxide with the oxide fraction increasing in discrete layers or continuously, and finally has an outer layer of pure oxide.

High efficiency turbines necessitate high inlet temperatures of about 1300° C. Some of the stationary and rotating components may be subjected to temperatures high enough to cause strength reduction or degradation through oxidation. Particularly susceptible areas are the combustion chamber and liners which have to be suitably protected /6/.

In one smaller turbine, Al-Si diffusion coating has been used as a thermal barrier. Diffusion coating application on large thin-walled components is not feasible, however.

Ability to apply ceramic coatings with properties to withstand thousands of thermal cycles without degradation is of particular advantage. Some of the coatings used as thermal barrier are aluminium oxide, zirconium oxide, and composite coatings based on magnesium zirconate /10/.

Ceramic coatings on their own tend to spall under thermal cycling. In the case of magnesium zirconate this drawback is overcome by applying a bond coat of Ni-Al-coating followed by an intermediate layer composed of a mixture of Ni-Al and magnesium zirconate. This intermediate coating has a coefficient of thermal expansion between magnesium zirconate and Ni-Al. Thus, a truly thermal barrier composite coating is achieved.

One typical example is that of an inner combustion chamber of a large turbine, see Fig. 10, where the whole outer surface is coated in three steps by the powder mentioned above. The microstructure of the coating is shown in Fig. 11.

Increased demands for higher gas turbine performance yielded the development of improved thermal barrier coatings. While multi-layer thermal barrier coating systems based on nickel-aluminium and nickel-chromium metallic components have provided good service in a number of applications, failures were observed to be caused by oxidation followed by exfoliation of the outer ceramic or intermediate transition layer /11/.

More recently, laboratory and experimental engine testing has indicated that improved service behaviour could be achieved by utilizing continuously graded layers /11/, where the metallic component is made of CoCrAlY alloy deposited as a bond coat followed by the gradual introduction of the ceramic component (magnesium zirconate) into the

powder stream. The top layer of the coating is of pure ceramic. It can be stated that, for the present time, this type of coating reveals optimum protection as thermal barrier coating applied in combustion chambers.

Furthermore, systems consisting of a plasma sprayed layer of zirconia stabilized with either yttria, magnesia or calcia over a thin alloy bond coat have been developed. Their potential was analyzed and their durability and benefits evaluated for application in a turbojet engine /9/. The coatings on air-cooled rotating blades were in good condition after completing as many as 500 two-minute cycles of engine operation between full power at a gas temperature of 1370°C and flame-out, or as mech as 150 hours of steady-state operation on cooled vanes and blades at gas temperatures as high as 1370°C with 35 start and stop cycles. On the basis of durability and processing cost, the yttria-stabilized zirconia was considered best of the three coatings investigated /9/. By this coating the measured mid-span leading-edge vane metal temperature in the research engine was reduced by 190 K - from 780° C for the uncoated vane to 590°C for the coated. Metallographic examination of the coating after cyclic testing showed that the NiCrAlY bond coat adhered well to the blade wall surfaces. However, cracks were detected in the calcia-stabilized zirconia coating, but did not cause spalling of the coating /9/.

## 5. WEAR AND CORROSION

When both corrosion and wear have to be encountered, the coating and the adjoining substrate surface need to be properly sealed and protected. One method of sealing a sprayed coating is by applying epoxy-primer type finish prior to grinding. This method has proved effective when hard coatings like tungsten carbide, chromium carbide etc. are sprayed onto aluminium and magnesium alloy components.

For proper adhesion of such type of sealing, sprayed coating porosity should not exceed about 15 % /6/.

Electroplating under certain conditions can be employed to seal sprayed coatings and protect the adjoining substrate surface. This method is particularly useful when an electroplate is specified as normal surface protection for the component and the coating is somewhat identical with the substrate in chemical composition. Nickel-aluminide coatings on low-alloy steels, chromium and austenitic stainless steels can be plated with nickel.

The surface activation and plating conditions as applicable to the substrate, also suffice for the coating. Caution has to be excercised in electroplating dissimilar coating-substrate combinations as preferential chemical attack may occur within the coating, and in the coating-substrate interface or at the substrate.

Tungsten carbide coating on chromium stainless steel when processed for nickel-plating showed preferential attack leading to carbide particles pull-out.

Wherever electroplating is applied the coating should be ground to fine finish in order to enable a uniform plate thickness /12/. Coatings with rough finishes are plated irregularly. Table 2 gives surface finishes practised on various substrate-coating combinations.

## 6. PROTECTIVE HOT GAS CORROSION COATINGS

Alloys of the MCrAlY-type are the basis for high temperature protection systems in gas turbines. 'M' can be one or more of Ni, Co or Fe.

At the present, the most applied method to deposit such coatings onto turbine rotor blades is physical vapor deposition (PVD). In the PVD process the coating is formed mostly by evaporation of atoms from one or more electron beam melted alloy sources. Development of Low Pressure Plasma Spraying (LPPS) in the last eight years now permits to deposit this kind of coatings by thermal spraying technique. Coatings free of oxides and nearly free of pores can be produced /13/. These are essential preconditions for successful application in gas turbines. The advantages of LPPS and investigations concerning creep performance and fatigue strength of MCrAlY coated by LPPS led to first commercial applications of such coatings in jet engines. Fig. 12 shows the creep performance of CoCrAlY coated blades compared with the performance of aluminized blades.

Blades coated with CoCrAlY by plasma spraying in vacuum exhibit approximately the same mechanical characteristics as aluminized blades. The vacuum plasma sprayed blades also show that, by etching the contact surface prior to spraying, better mechanical strength can be achieved than by peening.

It is generally recognized, however, that blades with sprayed protective coatings will show no improvement in terms of creep strength. This is attributed to the particular heat treatment during or after coating at temperatures of more than 1000° C. It is assumed that, with the IN 100 material, the carbide changes from $M_{23}C_6$- to $M_6C$-type in this temperature range. An improvement would be achieved by lowering the heating temperature to below 1000 ° C, which gives a diffusion zone with CoCrAlY of 5 to 7 µm deep /14/.

REFERENCES


| | | |
|---|---|---|
| / 1 / | Trsek, A.: | The use of thermal sprayed coatings for extended life of aircraft jet engine parts<br>8th International Thermal Spraying Conference, Miami 1976 |
| / 2 / | Messbacher, A.: | Thermisches Spritzen im Flugtriebwerkbau<br>wt-Z. ind. Fertig. 65 (1975), S. 619/624 |
| / 3 / | Levinstein, M.A. and R.K. Betts: | Thermal Spray Coatings in Aircraft Applications<br>6th International Metal Spraying Conference, Paris 1970 |
| / 4 / | Cook Jr., E. B.: | Coating Developments for the Gas Turbine Hot Section<br>Thirteenth Airlines Plating Forum, Dallas, Texas, February 1-3, 1977 |
| / 5 / | Bowen, K.E.: | The Application of Flame Sprayed Coating Technology in Aircraft Maintenance<br>in:<br>Scripts of Union Carbide, Ratingen, Germany |
| / 6 / | Malik, M.P.: | Application of Sprayed Coatings<br>Contribution to 7th International Thermal Spraying Conference, London 1973 |
| / 7 / | Jürgens, W.: | Thermisches Spritzen bei der Neufertigung und Instandsetzung von Flugtriebwerkteilen<br>DVS-Berichte 47, Thermische Spritztechnik 1977 |
| / 8 / | Shiembob, L.T.: | Development of a plasma sprayed ceramic gas path seal for high pressure turbine applications<br>Final Report, 2nd Oct. 1975 - 31th Dec. 1976<br>Nasa Cr-135183, PWA-5521 |
| / 9 / | Liebert, C.H. and F.S. Stepka: | Ceramic Thermal Barrier Coatings for Cooled Turbines<br>AAIA/SAE 12th Propulsion Conference, Palo Alto, California, July 26 - 29, 1976 |
| / 10 / | N. N.: | Metco Inc., Technical Bulletin "Magnesium zirconate powders" |
| / 11 / | Wilkins, C.R., F. J. Wallace and P.H. Zajchowski: | Ceramic/metallic thermal barrier coatings for gas turbine engines<br>8th International Thermal Spraying Conference, Miami 1976 |
| / 12 / | Malik, M.P.: | Applications of plasma metal spraying in salvaging aircraft and engine components<br>6th International Metal Spraying Conference, Paris 1970 |
| / 13 / | Steffens, H.-D.: | Sprayed Coatings<br>AGARD Lecture Series No. 106 |
| / 14 / | Messbacher, A. and W. Track: | Vacuum Plasma Spraying of Protective Hot Gas Corrosion Coatings<br>8th International Thermal Spraying Conference, Miami 1976 |

| Coating Designation | Coating Alloy Composition Weight % | | | | | | | | | | | Added Oxide Weight % | | Heat Treatment After Coating | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | First Stage | | | Second Stage | | |
| | Co | Cr | Ni | Mo | W | Ta | Al | Y | C | Si | V | $Al_2O_3$ | $Cr_2O_3$ | Temp. °C | Time Hours | Air or Vacuum | Temp. °C | Time Hours | Air or Vacuum |
| L-103 | 44 | 28 | 5 | | 19 | | | | 3 | | 1 | | 3 | 780 | 4 | Air | — | — | — |
| L-103A | 44 | 28 | 5 | | 19 | | | | 3 | | 1 | | 3 | 1080 | 4 | Vacuum | 788 | 4 | Air |
| LCO-17 | 55 | 25 | | | | 10 | 7 | 5 | 2 | | | 10 | | no heat treatment | | | | | |
| LCO-17A | 55 | 25 | | | | 10 | 7 | 5 | 2 | | | 10 | | 1080 | 4 | Vacuum | 898 | 4 | Air |
| LCO-19 | 57 | 30 | | | | 10 | | 5 | 2 | | | 10 | | no heat treatment | | | | | |
| LCO-19A | 57 | 30 | | | | 10 | | 5 | 2 | | | 10 | | 1080 | 4 | Vacuum | 898 | 4 | Air |
| LC-1B | 75 % $Cr_3C_2$ + 25 % NiCr | | | | | | | | | | | | | no heat treatment | | | | | |

Table 1: Coating chemistry and heat treatment processes of new high temperature wear resistant coatings [5]

| Substrate Metal | Coating Material or Type | Final Surface Protection |
|---|---|---|
| Low alloy high strength steels | Nickel-aluminide | Cadmium plate<br>Epoxy-primer plus paint |
| Low alloy steel | Low alloy steel | Cadmium, Chromium or Nickel plate |
| Chromium stainless steel | Nickel-aluminide | Nickel or Cadmium plate |
| Aluminium alloy 7075, 7079 types | Aluminium alloy 7000-type | Chemical conversion<br>Anodize<br>Primer and Paint |
| Austenitic stainless steel | Austenitic stainless steel | Passivation<br>Cadmium or Nickel Plate |
| Aluminium alloys 2024 or 7075 types | Tungsten Carbide | Sealing with epoxy primer before grinding plus painting of non-sliding areas |

Table 2: Surface finishing of coated parts [6]

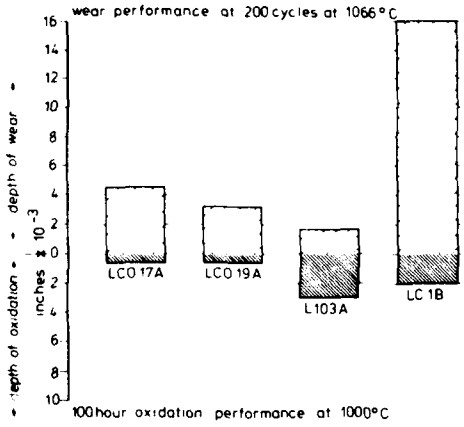


Fig. 1: Wear and oxidation resistance of cobalt base coatings [5]

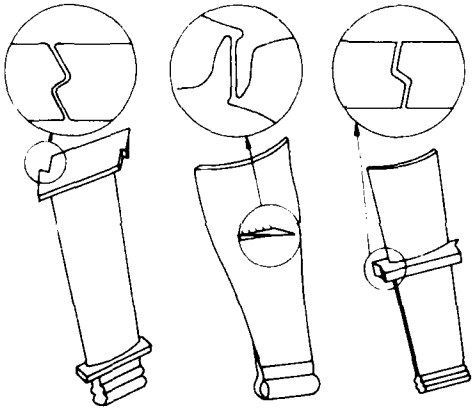

Fig. 2: Interlock applications for hard-surfacing coatings [3]

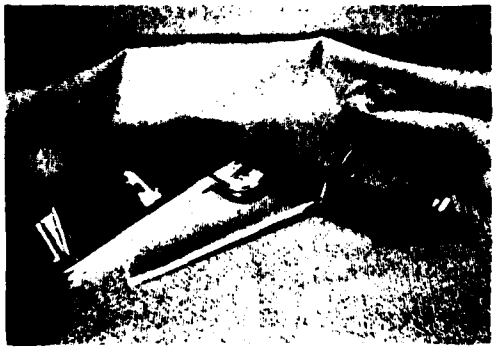

Fig. 3: Detonation-gun coated compressor blade [4]

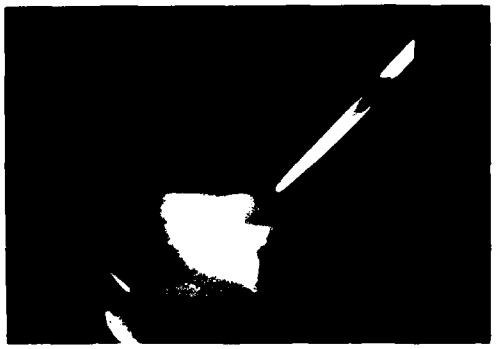

Fig. 4: Detonation-[illegible] in operation (Union Carbide)

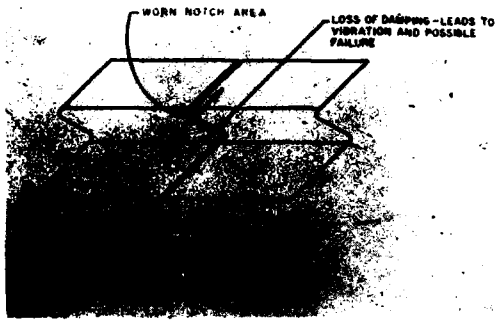


Fig. 5: Effect of notch wear (turbine blade shroud; Union Carbide)

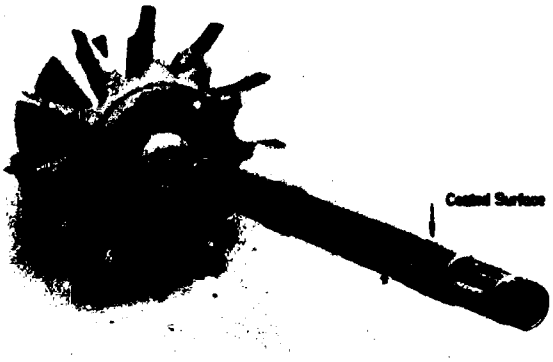


Fig. 6: Rotor wheel shaft (Ti-6Al-4V) [6]

Fig. 7: Lugs of the main landing gear, outer cylinder

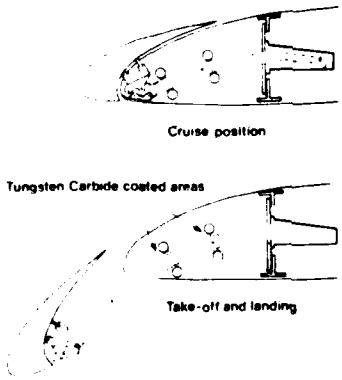


Fig. 8: DC-9 wing slat track system [5]

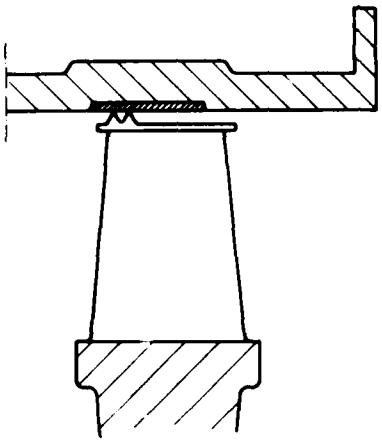

Fig. 9: Principle of abradable gas path seal

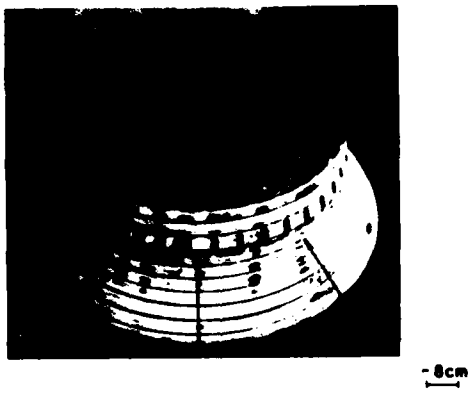


Fig. 10: Inner combustion chamber [6]

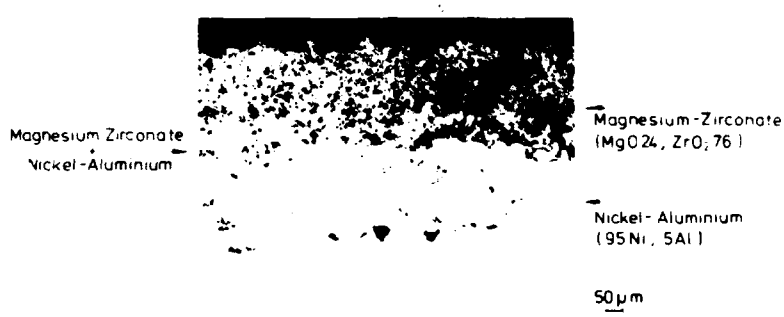


Fig. 11: Transverse micro-section of a three layer thermal barrier coating [6]

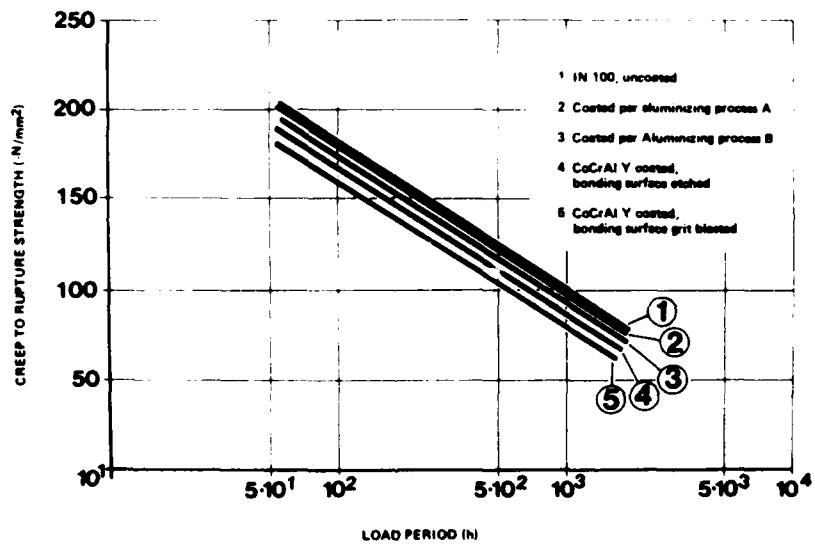


Fig. 12: Creep rupture strength of uncoated and coated turbine rotor blades in IN 100 cast nickel alloy at 950 °C in hot gas atmosphere [14]

# WEAR RESISTANT COATINGS MADE BY CHEMICAL VAPOUR DEPOSITION

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## ABSTRACT

A very important application of chemical vapour deposition is the formation of hard layers for wear resistance. The technique is well established as a commercial process for coating steel and hardmetal tools with titanium carbide and nitride. However, the use of other hard materials such as chromium carbide and tungsten carbide is being developed for specific applications.

The operating temperatures of the established hard coating processes are in the range 800-1000°C. This is an advantage in that good diffusion and bonding may develop, but it is a disadvantage in that steel substrates require re-hardening after coating. Current research is directed at reducing the deposition temperatures without loss of good adhesion and wear properties.

This paper reviews the methods by which hard layers are formed by chemical vapour deposition, and discusses the properties of these hard materials. The economics of chemical vapour deposition are also discussed because this is an extremely attractive aspect of the process for large batches of small components.

## 1. INTRODUCTION

Protection against wear through surface hardening is a very old technology indeed, embracing carburising, nitriding etc. More sophisticated diffusion techniques have been developed over the years, such as plasma nitriding, carbonitriding, siliconising, with very hard overlay-type coatings becoming increasingly important. The overlay coatings include carbides, oxides, nitrides and borides with the common property of extremely high hardness. Wear resistance is also affected by mutual solubility of the parts in contact, their coeeficient of friction and also their corrosion resistance.

The earliest uses of the very hard coatings of $Cr_7C_3$ and TiC go back to the early 1960's (1,2) with applications on steels. Since that time the coating of throw-away cutting tips has become a major industrial application (3). The coating of steels is now becoming increasingly important as well.

## 2. SUBSTRATE EFFECTS

The relationship between coating and substrate is extremely important in wear resistance. The modulus and hardness of both parts and the bond between them all contribute to the ultimate wear resistance. Two general types of effect can occur. The first is an interaction between the developing layer and the second is the effect of the CVD treatment temperature on the substrate material itself.

At the elevated temperatures where most CVD treatments are carried out, diffusion effects can be anticipated. These are put to advantage in such standard treatments as nitriding and boronizing. However the effects are not necessarily advantageous, and possibly the best-known problem occurs in the development of the so-called η-phase when coating cemented carbide cutting tips. Cemented carbides consist primarily of WC particles sintered together with some 5 - 10 vol % Co.

During the CVD process where a TiC layer is formed, some of the necessary carbon is drawn from the substrate in the very early stages of coating. As is clear from the phase diagram in Fig. 1a decarburization of Co-WC alloys leads to the formation of η-phase under the carbide coating, as shown in Fig. 1b. This phase is usually of the type $M_6C$ or $M_{12}C$ (4,5) depending on the treatment temperature and a volume contraction, hence porosity, accompanies its formation. In practical terms the phase causes a loss in bend strength of the coated tip(6) which can be as high as 50%. Some slight degree of η-phase is probably insignificant but is usually prevented by carburizing the substrate before the CVD-TiC treatment(7). A detailed analysis of the sintered carbide/hard coating transition(8,9) shows decarburization effects to be present in both CVD and activated reactive evaporated (ARE) samples, even in the absence of η-phase. An example of where carbon is intentionally drawn from the steel to form a carbide layer was discussed before - chromium carbide $Cr_7C_3$. If the carbon content of the steel is such that primary cementite exists in it, then a cementite interlayer can develop under the carbide coating. This has been observed with vanadium (Fig. 2.), chromium and titanium carbides on high carbon steels. In a similar fashion an intermediate layer of chromium carbide can form under a TiC coating on steels containing large amounts of chromium, e.g. the 12% Cr ledeburitic steels.

Diffusion of the coating material into the substrate can also occur. The loss of carbon from the steel in chromium carbide formation finds its counterpart in the diffusion of chromium into the steel. In the specific case of a low carbon steel substrate, the chromium enrichment of its surface (or any other steel-alloying element) shifts the eutectoid point (Fig. 3a) to lower carbon levels. Consequently, there is an increase in the apparent perlite content just under the carbide coating (Fig. 3b), although the steel has in fact lost carbon. Hence, decarburization effects are not easily avoided when coating steels with carbides.

A completely different aspect of CVD coating of steels is their response to the thermal treatment itself. The basic CVD treatment is carried out at the austenitizing temperature of many steels 900 - 1050°C. The different phases which can exist in steel have different volumes (Table 1) so that dimensional changes will occur after the CVD and subsequent tempering treatments. Careful handling can hold tolerances to better than 0,05% (i.e. 50 μm per 100mm diameter). The precise changes are difficult to predict as they depend on treatment temperature, coating speed and the existence of any degree of preferred orientation (10). As the coatings tend to oxidize at elevated temperatures, water quenching or tempering in air are precluded. Only oil or inert atmosphere quenching steels can be employed.

## 3. CEMENTED CARBIDE CUTTING TOOLS

Indexable cutting tool tips are probably the major industrial application of the CVD process. Approximately 30% of the tips used in the auto industry are coated. Depending very much upon the cutting conditions, such as substrate type, cutting speed and whether the cutting is continuous or not, a general improvement in tool life of 2 - 5 times can be expected. This is quite a remarkable increase in lifetime for a price increase of only 10% (quoted by a reputable Swiss manufacturer).

Tips are manufactured in a wide array of shapes (Fig. 4) and are normally graded by shape and by application, but not by composition, following ISO shape and application codes. Tips supplied in the same application grade by different manufacturers may well be of different composition and grain size, but have nominally the same cutting properties. The K series are normally simple WC-Co for machining short-chip steels and non-ferrous metals, the M series contain other carbides also and are used for most steels and high temperature alloys whilst the P series are highly carbide alloyed for steels producing long chips. Within each series a number is allocated to a grade which increases with increasing toughness but decreasing wear resistance.

Coated tips have more flexibility in their use than the uncoated variety. A typical manufacturer recommends the same grade of coated tips for all applications which would otherwise be met with K10-K20 and P20-P40 uncoated grades.

During a machining operation, wear on the tool tip (Fig. 5) occurs in two principal places: crater wear on the rake face adjacent to the tip and flank wear on the face adjacent to the work piece. The latter is simply due to mechanical rubbing against the work piece whereas the former is the result of uneven wear from the machined chip. It occurs because there is a diffusion reaction between the hot chip and the tungsten carbide in the tool[11]. As the solubility of iron in TiC is very much less than in WC, this diffusion wear is very much reduced. In addition, the energy involved in the machining operation is largely carried away by the chip so that temperatures of the order of 1000°C can develop in the crater. The lower frictional coefficient of the TiC coating reduces this heating. The coatings are more effective at higher cutting speeds where heating is greater.

The thickness of the TiC coating is also significant because the bend strength falls with increasing thickness[6]. It is found that an optimum thickness is of the order of 6 - 8 μm.

An alternative coating to TiC is the golden coloured TiN. It is less hard (2270 Hv compared with 3450 Hv), but has good chemical and corrosion resistance. It dissolves even less iron than does TiC so that diffusional wear is further reduced; this, taken together with a better hot hardness, yields a better coating resistance. In contrast the lower hardness gives a poorer resistance to flank wear than a TiC coating. The best properties have been sought by a layered coating with TiC under TiN or by making a mixed Ti (CN) coating[12].

Recently a further development has occurred whereby $\alpha$-$Al_2O_3$ coating is either put directly on the cemented carbide or on an intermediate TiC layer[13]. $Al_2O_3$ has a hardness of about 2,500-3,000 Hv with a very low coefficient of friction and excellent oxidation resistance. The resulting lifetime increase over the TiC/TiN coating is a further factor of two or more, depending upon the cutting speed. A fracture section scanning electron microstructure of a TiC/$Al_2O_3$ coated cemented carbide is shown in Fig. 6.

The increased resistance to wear and oxidation afforded by the $Al_2O_3$ coating and also by a parallel Ti(CNO) development[14] allowed cutting speed to be increased. Results of some machining tests using coated K10-K20 grades are shown in Fig. 7 where the improvement due to the oxidation resistant coatings is quite apparent. It is interesting to note that the flank wear remains quite low even after extended use to that the surface quality of the work-piece remains quite high.

## 4. TOOL STEELS

The use of TiC to protect tools from wear is becoming an application of increasing

interest. Whereas cemented carbides can be coated without any consideration for the substrate except for the formation of the η phase, steels require care because of shape changes associated with quenching and tempering. Many tools are made from either high speed steel or the 12% Cr ledeburitic tool steels. Neither shows excessive volume changes and both can be heat-treated at the conventional CVD treatment temperatures. In addition, the coefficients of thermal expansion are comparable: some 12 x $10^{-6}$ for steel and 8 x $10^{-6}$ for TiC, so that thermal contraction on cooling does not affect coating adhesion detrimentally.

Most tools used in cold work processes such as deep drawing, punching and cutting, do not become as hot as the carbide cutting tips so that diffusion wear can be regulated. The high hardness of TiC is its most important property and accounts for its frequent use. In corrosive environments where chemical attack may be significant, chromium carbide $Cr_7C_3$ (hardness 2250 $H_v$) is often used with vanadium carbide[16] as an alternative with intermediate corrosion resistance and hardness (2630 $H_v$).

The TiC coating thickness normally applied is of the order 6-8μm. The surface roughness of the tool should not exceed 30-50% of the coating thickness, so that high polished (often diamond lapped) tools with $R_t$ = 3μm are normally coated.

A completely different approach to the hard coating of steel is provided by the CVD of tungsten carbide.[16]. Tungsten carbide in the form of $W_2C$ is obtained by the reaction between tungsten hexafluoride, benzene and hydrogen at reduced pressures in the temperature range 325-600°C.

$$WF_6 + C_6H_6 + H_2 \rightarrow W_2C + HF$$

The deposit of tungsten carbide can be built up to a thickness of about 50μm before internal stresses cause spalling, but in general the coating has better mechanical properties when applied at a thickness of 10-20μm. The hardness of $W_2C$ is about 2300 $H_v$, which is substantially harder than sintered tungsten carbide because it is a pure carbide without any binder phase. It has a columnar structure which becomes more distinct as the coating thickness increases. The bonding between the tungsten carbide and the steel is generally achieved by the use of a nickel interlayer. There is no diffusional bonding at the process temperature and the overall bond strength is always less than that achieved by the high temperature processes.

$W_2C$ coatings offer the possibility of applying a hard surface to a fully-finished steel component without any loss of dimensional control. Moreover, this coating can be applied in a layer thick enough to allow a small margin for a final grinding operation after coating. However, the bond between the substrate and the coating is limited because no diffusion occurs at the low deposition temperature. The applications for which the $W_2C$ coating is best suited are those which principally involve abrasive wear. Such a device is the Mercer air plug gauge (Figure 8) which measures the diameter of holes very accurately. Compressed air is forced out of small holes in the body of the gauge so that it escapes through the narrow gap between the gauge body and the hole. The back pressure thus generated gives a measure of the gap, and hence, provided the gauge is accurately made, a measure of the hole diameter. The gauge needs a hard body to resist accidental scratches and incidental abrasion caused by particles in the air blown over it. Other measuring devices require similar protection, and also there are numerous textile-machine components which benefit from hard surfacing. Another successful application of $W_2C$ is in the coating of steel dies for the extrusion of aluminium (Figure 10).

Table 2 shows the results of a comparative abrasive wear test for CVD coated steels (17). The wear resistance of the coatings is in the order of their hardness, although it should be noted that a borided surface may still have a better life than a TiC coating simply because it is thicker.

## 5. ECONOMICS OF CVD FOR TOOLS

The effect of the CVD coating on the economics of cold working operations is best considered in the light of specific examples. The economics have to take the cost of producing the tool itself into account. This can be broken down:

a) cost of the steel itself.
b) cost of tool preparation, turning, grinding, milling, lapping and polishing.
c) cost of primary heat-treatment, hardening and tempering according to standard specifications.

It is clear that the production cost of a tool can vary very much according to its type and geometrical shape. Consequently the relative contribution of the CVD coating cost to the total becomes a subjective matter; the actual coating cost is normally calculated according to the volume of the tool. In general, tools which are both cheap and easy to make are coated more seldom than tools which are very expensive to produce.

Two examples of economic viability are discussed in terms of the approximate costs:

Example 1: Tooling costs of a mould for plastic (Fig. 10a) with dimensions approximately 80 x 170 x 22 mm = 300 $cm^3$

| | | |
|---|---|---|
| manufacture | 450.-- FrS | |
| CVD coating | 175.-- FrS | |
| total | 625.-- FrS | lifetime increase x5 - x8 |

Example 2: Tooling costs for a drawing mandrel (Fig. 10b) with dimensions 80mm Ø and 60mm long = 300 $cm^3$

| | | |
|---|---|---|
| manufacture | 85.-- FrS | |
| CVD coating | 175.-- FrS | (as above) |
| total | 260.-- FrS | lifetime increase x12 - x15 |

The crux of the decision as to whether the CVD coating is economically worthwhile is the increased performance or lifetime of the coated tool. In example 1 the coating costs are about 28% of the total. The increase in lifetime of 500-800% or even more reduces the contribution of the tool to the total cost per part produced, quite significantly:

625.-- FrS with 8 x life increase →
17.4% of the original tooling cost per part.

In example 2 (a drawing die for an alternator housing), the CVD costs are relatively much higher at 67% of the total. Even in this case the coating is still economically viable as tool performance is increased by 12-15 times. Thus the costs are reduced:

260.-- FrS with 15 x life increase →
20.4% of the original tooling cost per part.

In addition to the direct saving in cost, the CVD coating retains dimensional precision completely during the useful life of the tool because, in the absence of damage, the tool wear is effectively zero. This also means that the periodic checks of the dimensions of the housing can be omitted until signs of coating failure: cold-welding, cutting edge pick-up or drawing grooves are found on the parts produced. This leads to the immediate replacement of the tool.

It should be added that the costs associated with machine down-time and production loss during tool change and those resulting from the saving in tool-maker time are not included in the above analyses. Extreme cases are known where factories employ 1 or 2 tool-makers simply for tool maintenance involving the removal of adhesion damage etc. The coated tools can also contribute to reducing overheads, for example, an up to 80% reduction in lubrication costs.

There are cases where the economic situation is not quite so simple, where the carbide coating allows the possibility of reconditioning a tool. Tool reconditioning depends entirely on the wear which has occurred in relation to the required tolerance. Sometimes a tool can be simply repolished and re-coated. However, it is often the case that the tool tolerances are so fine that no such tool salvage is possible.

Example 3 examines the case of a follow-on tool as used in sequential deep drawing operations (Fig. 10c). The sequence is as follows: the die of smallest internal diameter is CVD treated; this is the one carrying the largest load and is also the most critical. As soon as the die is worn, it is ground to the (larger internal) diameter of the immediately preceeding step and again CVD coated. An example of such a sequence is in the production of shock absorbers. As the ledeburitic tool steels can be reheat-treated without significant overaging such tools can be re-used for up to five times. The tooling costs can be analysed as follows:

| | | |
|---|---|---|
| manufacture | 85.-- FrS | |
| CVD coating (5 times 108) | 540.-- FrS | (including re-grinding) |
| total | 625.-- FrS | |

the lifetime increase of a single tool is 40 times (i.e. 8 x per CVD operation):

625.-- FrS with 40 x life increase →
18.3% of the original tooling cost per part.

Considering the actual costs per part, we consider the equivalent comparison of 5 untreated dies with 1 die CVD coated 5 times:

| | | |
|---|---|---|
| tool cost without CVD | 425.-- FrS | |
| production | 10,500 parts | |
| tooling cost/part | 0.04 FrS | |
| tool cost with CVD | 625.-- FrS | |
| production | 84,000 parts | (factor 8x) |
| tooling cost/part | 0.0074 FrS | |

## CASE STUDIES

We now examine briefly some further examples of CVD applications.

Case I concerns the massive deep drawing punches shown in Fig. 11; they are used to manufacture shock absorbers from steel sheet. The punches are 98-160mm in diameter made from a ledeburitic DIN 1.2379 steel (X155 CrVMo 12 1) and coated with 8-10μm of TiC.

The tool life-time is increased:
without TiC coating 900-1000 parts
with TiC coating 150,000-200,000 parts
which is factor of about 200 times. If account is taken of the reduction in down-time and its associated loss of production, the increase in productivity per punch is astonishing.

To be realistic, such punches are never used without some form of surface treatment. The best alternative gives a lifetime of some 5,000 parts, so there is still a relative improvement of some 40 times. Further, the alternatively infinite lifetime, is uneconomic not only because of the inherent cost but also because the design and tooling of most cars is effectively changed each year.

Case II concerns the coating of the wedge-pieces in reverse locking clutches. These are arrowed in Fig. 12a; they are made from a DIN 1.3503 steel (100 Cr 6) and are coated with a $Cr_7C_3$ carbide which, although microstructurally columnar, is of random crystallographic orientation.

The mode of operation of the clutch is to rotate freely in one direction but to lock firmly in the other. In the forward direction the action between the wedge pieces and the shaft is sliding friction - normal wear conditions. In the reverse direction the pieces lock and a high shear stress acts at the contact points. A coating is required with excellent wear resistance and good adhesion to the steel substrate. Further the coating should not be so hard that the running surface becomes damaged by it when the clutch does not lock at all. This combination of properties can be achieved ideally with chromium carbide. The microhardness is high enough for good wear resistance in spite of the rather high coefficient of friction 0.69 but does not damage the running surface when locked.

From an economic point of view, the increase in lifetime is compared to the coating costs in Fig. 12b. A moderate cost increase leads to a lifetime increase of a factor of 20 times.

## REFERENCES


1. S. Cseh, Proc. 1st Int. Symp. "Metallkunde u. Warmebehandlung" 1967, Warsaw, Paper B12.
2. W. Ruppert, Metalloberflache 1960 14 193.
3. H.E. Hintermann and H. Gass, Schweiz. Archiv, 1967 33 157.
4. W.D. Sproul and M.H. Richman, J. Vac. Sci. Tech. 1975, 12, 841.
5. H.E. Hintermann, H. Gass and J.N. Lindstrom, Int. Conf. CVD III, 1972, [illegible], Am. Nuc. Soc.
6. W. Schintlmeister, O. Pacher, K. Pfaffinger and T. Raine, J. Electrochem. Soc., 1976, 123, 924.
7. V.F. Sarin and J.N. Lindstrom. Proc. 6th Int. CVD Conf. Atlanta 1977, Electrochem. Soc., Princeton, 1977, 389.
8. N.K. Sharma, W.S. Williams, and R.J. Gottschall, Thin Solid Films, 1977, 45 265.
9. N.K. Sharma and W.S. Williams, ibid, 1978, 54, 75.
10. W. Ruppert, Thin Solid Films, 1977, 40, 27.
11. E.M. Trent, Proc. IME 1952, 166 64.
12. W. Schintlmeister and O. Pacher, J. Vac. Sci. Tech. 1975, 12, 743.
13. R. Funk, H. Schachner, C. Triquet, M. Kornmann and B. Lux, J. Electrochem. Soc. 1976, 123 285.
14. T. Sadahiro, S. Yamaya, K. Shibuki and N. Vjlie, Proc. 9th Plansee Seminar, Reutte 1977, paper 32.
15. G. Ebersbach, E. Mey and G. Ullrich, die Technik, 1974, 29 273.
16. R.H. Lewin and C. Hayman, British Patent No. 1,326,769 (1973).
17. K.K. Yee, Int. Met. Revs. 1978, 1, 19.

TABLE 1

Specific volume of phases in steel

| Phase | Specific volume $cm^3/gm$ (at 20°C) |
|---|---|
| Austenite | 0.1212 + 0.0033 x (% C) |
| Martensite (lower bainite) | 0.1271 + 0.0025 x (% C) |
| Cementite | 0.130 |
| Ferrite + cementite (pearlite or upper bainite) | 0.1271 + 0.0005 x (% C) |

TABLE 2

Abrasive wear results of some coated and uncoated materials

| Test material | Treatment or coating† | Hardness (HV) | Relative volumetric wear |
|---|---|---|---|
| Chemical vapour deposition | | | |
| 105WCr6 | TiC (1050°C) 12 µm | 3200 | 3.5 |
| C100 | $W_2C$ (550°C) 30 µm | 1900 | 4.8 |
| 100Cr6 | Vanadized 30 µm (1100°C) | 2400 | 7.5 |
| C100 | Vanadized 30 µm (1100°C) | 2400 | 9 |
| C100 | Borided 100 µm ( 900°C) | 1600 | 12 |
| 100Cr6 | Borided 100 µm ( 900°C) | 1600 | 14 |
| Ck15 | Borided 100 µm ( 900°C) | 1600 | 30 |

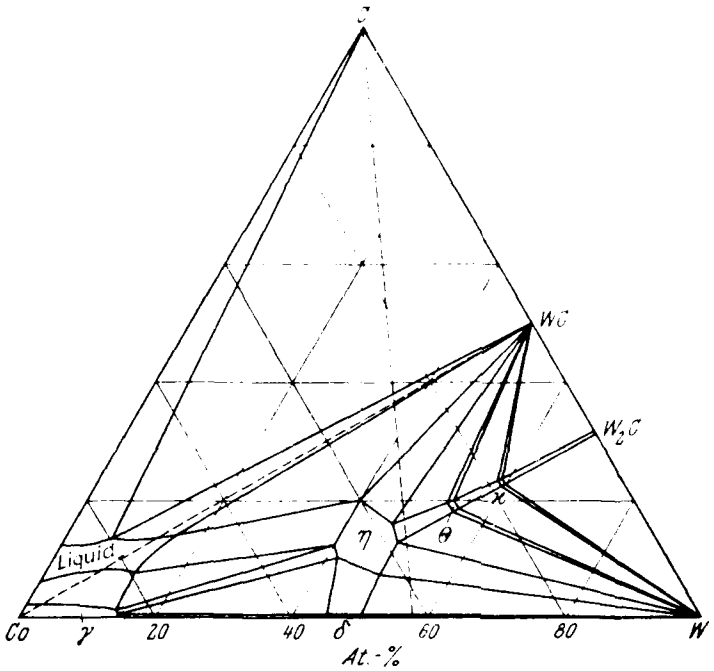


Fig. 1a. Co-W-C phase diagram at 1400°C (after P. Rantala and J.T. Norton, 1st Plansee Sem. 1952 p. 303).

Fig. 1b. TiC coated cemented carbide containing particles of dark etching η-phase (courtesy Berna-Bernex A6). (x 1000)

Fig. 2. Steel containing 1.45% C vanadized at 1020°C showing the VC coating with a $Fe_3C$ interlayer. (x 600)

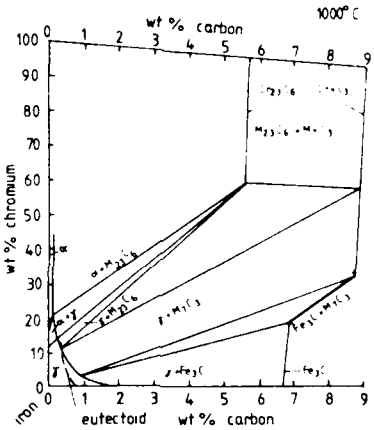


Fig. 3a. Fe-Cr-C phase diagram at 1000°C.

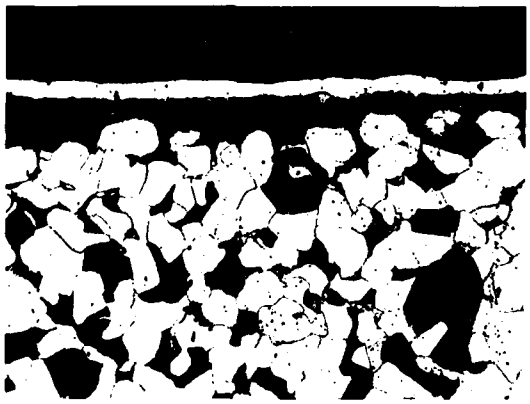

Fig. 3b. Steel containing 0.45% C chromized at 1010°C showing $Cr_7C_3$ coating and an apparent pearlite increase directly under the coating caused by the shift in the eutectoid point following chromium absorption. (x 500)

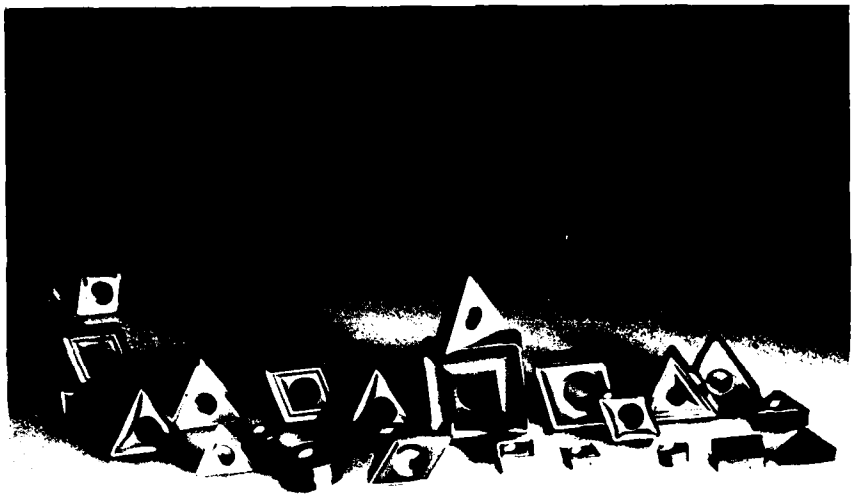

Fig. 4. A selection of coated cemented carbide cutting tool inserts (courtesy Stellram SA).

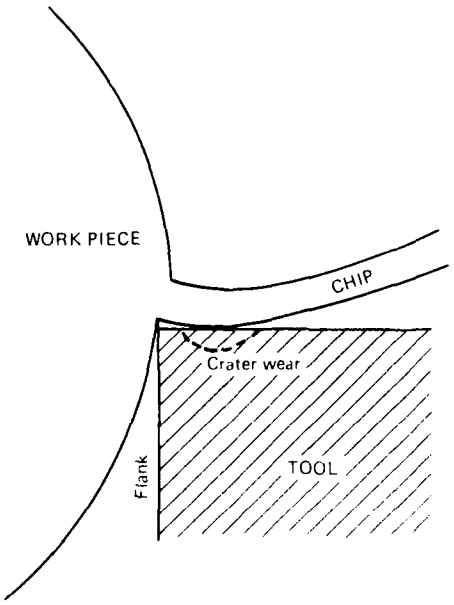


Fig. 5. Schematic diagram of machining showing the wear phenomena on the flank and rake faces of the cutting tool.

Fig. 6. Scanning electron micrograph of a fracture section showing the thin (light coloured) outer layer of $\alpha$-$Al_2O_3$ over the fine-grained TiC coating on a cemented carbide cutting tool. (x 2,500)

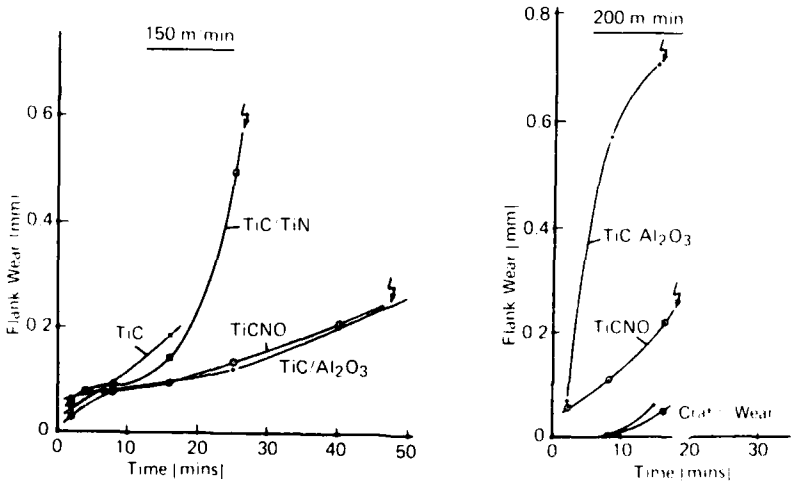


Fig. 7. Flank wear during the machining of 0.75% C steel with variously coated K10 or K20 150 code insets.

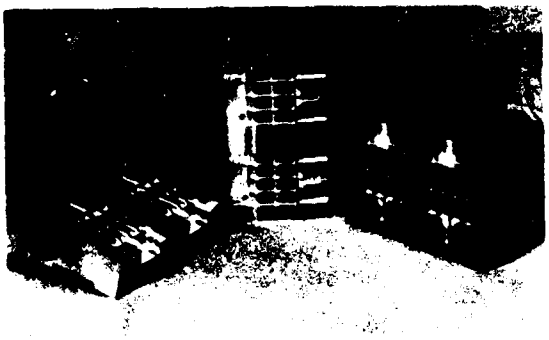

Fig. 10a. TiC coated mould for plastics.

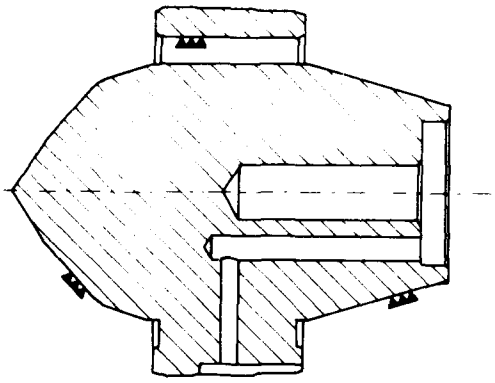

Fig. 10b. Drawing mandrel for alternator housings.

Fig. 10c. Follow-on tools coated with chromium carbide.

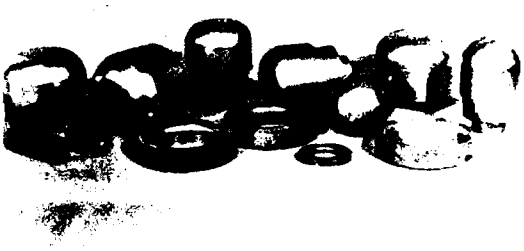

Fig. 11. TiC coated punches and matrices (ledeburitic 12% Cr steel DIN 1.237a) for deep drawing steel sheet. The working surface of the punches lies in the diamter range of 98-160mm.

Fig. 12a. A reverse locking clutch assembly with part of the outer case removed to show the wedge pieces which are coated with chromium carbide.

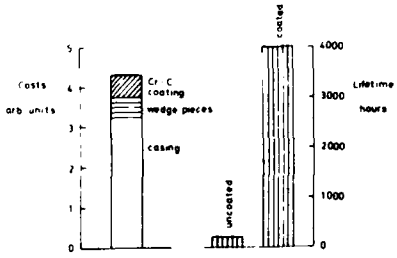


Fig. 12b. A comparison between the costs of the complete casing, wedge pieces and carbide coating of the clutch shown in a). Also shown is the average life-times of the wedge pieces in coated and uncoated conditions.

# APPLICATIONS OF PHYSICAL VAPOR DEPOSITION PROCESSES

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Summary

The applications of Physical Vapor Deposition processes are discussed. They are coatings for decorative applications, heat/energy barriers, microelectronic devices, corrosion of aircraft parts, high temperature corrosion, tribological phenomena, cutting tools, optical components, thin transparent conductive layers, and materials conservation. The fabrication on self-supporting shapes and potential applications are given.

## I. INTRODUCTION

At the outset, it would be useful to restate the factors which make the Physical Vapor Deposition Processes very attractive for numerous current and future applications. They are:

1) Virtually any metal, alloy and ceramic coatings as well as some polymeric coatings can be deposited.

2) The deposit can be a free-standing shape or a coating.

3) These overlay coatings are non-equilibrium coatings thus making them virtually independent of the substrate material unlike diffusion coatings.

4) The substrate temperature can be varied over a wide range thus permitting the deposition of coatings onto substrates which may degrade by high temperature exposure.

5) The adhesion of the coatings is excellent.

6) The surface finish is equal to that of the substrate thus virtually eliminating any need for post deposition grinding or polishing operations.

7) The deposition rate can be varied from low to high which makes large scale high rate production possible.

8) None of the PVD processes create or use toxic materials unlike electrodeposition and therefore do not present any ecology problems.

The deposition apparatus can be batch type or capable of continuous deposition. Examples of batch type evaporation and sputtering units are well known. For high production rates, one goes to the following:

1) A fast cycle coater which is the sequential coating of a given number of substrates without opening up the system to the atmosphere. It consists of a deposition chamber connected through vacuum values to a substrate holding chamber and a coated substrate receiving chamber as shown in Fig. 1. The substrates mounted on a tray are coated and moved into the receiving chamber. Thus a large number of substrates can be coated without having to open the evaporation chamber to atmosphere.

2) A semi-continuous in-line system where the substrates are transported from one chamber to the next for the different steps involved in a coating operation as shown in Fig. 2. The substrates spend a finite amount of time in each chamber. Alternately, a given length of sheet or foil is stored inside a vacuum chamber uncoiled coated by evaporation and recoiled.

3) A continuous in-line system as shown in Fig. 3 where the substrate normally in the form of strip, sheet, or foil goes through a staged series of differentially pumped chambers at various pressures to enter and exit the evaporation chamber which is at high vacuum.

## II. CLASSIFICATION OF APPLICATIONS

The applications of Physical Vapor Deposition processes may be classified into two generic types:

1) Free standing shapes such as sheet, foil, or tubing. In this case the material is deposited onto a substrate and subsequently released from it by the use of a parting agent deposited onto the substrate before coating.

2) Thin and thick films.

The applications are very widespread and for convenience may be classified as follows as per the proposal by Smith [1]:

Decorative: Automotive trim (interior and exterior), toys, cosmetic packaging, pens and pencils, Christmas decorations, food and drink labels, costume jewelry, home hardware, eyeglass frames, packaging and wrapping materials, watch cases and bands.

Optically Functional: Laser optics (reflective and transmitting), architectural glazing, home mirrors, automotive rear view mirrors, eyeglass lenses, projector reflectors, camera lenses and filters, instrument optics, auto headlight reflectors, TV camera optical elements, meter faces.

Electrically Functional: Semiconductor devices, integrated circuits, capacitors, resistors, magnetic tape, disc memories, superconductors, electrostatic shielding, switch contacts, solar cells.

Mechanically Functional: Aircraft engine parts, aircraft landing gear, solid film lubricants, hard coatings on cutting tools.

Chemically Functional: Corrosion resistant fasteners, gas turbine engines, blades and vanes, battery strips, marine use equipment.

III. DECORATIVE APPLICATIONS

This is a large world-wide industry. The earliest applications involved the coatings of various polymeric items such as buttons, toys, tinsel, upholstery fabric with aluminum followed by anodization and/or dyeing of the coating to various bright colors.

The technology has now been extended into functional decorative coatings on watches and automobile parts. Watch cases and bands made of carbide or high speed steel are being plated with titanium nitride coatings having a golden luster and a high scratch resistance due to their high hardness which makes them superior to electroplated gold coatings. The process is used in Reactive Ion Plating.

The energy crisis has brought about a great impetus to decrease the weight of automobiles. As a result, various heavy automobile parts such as grills, headlight bezels, etc. are being made out of plastic with a thin chromium overlay coating for the shiny look, replacing cast metal parts with electroplated chromium coatings.

A large production coating facility was built by the Varian Palo Alto Vacuum Division and is presently being used to deposit metal decorative coatings onto plastic automotive parts. The parts are loaded on trays which pass through vacuum interlocks and under an array of twenty-four magnetron type sputtering sources. The tray size is typically 0.9 m (34 inches) wide by 2.2 m (86 inches) long. The production throughput (based on tray area) for a chromium coating thickness of about 75 mm (750 Å) is 74 $m^2$ (800 $ft^2$) per hour or about 300,000 $m^2$ (3 to 4 million $ft^2$) per year on a three-shift basis.

IV. HEAT/ENERGY BARRIER COATINGS

Sheets of polymeric material such as mylar are being continuously coated with aluminum at high rates using electron beam evaporation in an air-to-air line. The product is used for packaging, light weight thermal insulation, etc.

The same technology conceivably may be used in the future to produce light weight high reflectance films for large solar reflector arrays to be deployed in space.

A very large use of such coatings is in altering the transmission and reflection properties of glass to be used in architectureal and automotive applications. Conventionally, the glass manufacturers used to alter such properties by changing the actual glass composition to obtain such products as grey and bronze glasses. The desirable method would be to have a standard low cost glass and change the properties with single or multilayer overlay coatings. This has blossomed into a major product line in the last ten years. The pioneering work was carried out by the Libby-Owens-Ford Co. who designed and operate a large scale semicontinuous evaporation to coat panes of glass 10 ft × 12 ft. The size and weight of the glass is such that it has to be hung in a vertical plane [2]. Two plates of glass back-to-back are attached to a carrier frame and moved through the coating chamber continuously past a number of specially designed 150 KW electron beam evaporation sources projecting the upper flux in a horizontal direction at a speed from 1 to 100 inches per minute [3]. The specifications of the evaporator are:

1) an electron gun with a filament life of a year or more;
2) a method of feeding the source material that would operate under high vacuum;
3) large area, high evaporant flux sources for horizintal evaporation;
4) a source configuration that would coat 120×144 in. substrates with a uniform coating while utilizing a reasonable source-to substrate distance;
5) reliable vacuum evaporation and film thickness monitoring systems.

In order to appreciate some of the problems encountered in controlling multilayer coatings on ten by twelve foot substrates in a semicontinuous system, a brief description of the actual system is needed. The system is divided into six separate chambers as follows: 1) initial pumpdown; 2) glow cleaning and isolation; 3) heat and isolation; 4) coating; 5) cooling and isolation; and 6) vent to atmosphere. The system is set up to coat two substrates at a time. This is done by loading the substrates in an overhead carrier in a back-to-back relation and having evaporation sources mounted on both sides of the coating chamber. There are three banks of sources on each side making one, two, or three-layer films possible. Chambers one and six are capable of pumping from atmosphere to 50 microns in 100 seconds. The pressure in the coating chamber is held at 3 to 5 × $10^{-6}$ torr with a base of 3 × $10^{-7}$ torr possible by means of twelve 48" 95,000-liter/second diffusion pumps.

More recently, sputtering systems have become the vogue for coatings on architectural glass. Thornton has recently published a discussion of these developments which are given below [4].

Figure 2 shows a schematic diagram of a typical in-line production system. Flat plate substrates or trays containing substrates pass on rollers into an entry-lock vacuum chamber. After evacuation to a pressure of the order of 1 to 10 Pa ($10^{-1}$ to $10^{-2}$ torr), they are passed into a buffer chamber and a new plate is introduced into the entry-lock chamber. Vacuum conditions in the buffer chamber can be adjusted to match those in the coating chamber, so that the perturbation to the coating chamber is minimized when the plates enter. Baffles and differential pumpting can be used for this purpose. When the buffer-to-coating chamber valve is opened, the substrates are quickly inserted into the coating chamber, where they are transported at a slower and controlled speed by an array of sputtering sources which may be configured to deposit a single or multilayer coating. An essential feature of such an apparatus is that relatively little additional complexity is added in going from a single layer to a multilayer coating. With suitable baffling and differential pumping, metal and reactive sputtering can be accomplished using cathodes in relatively close proximity to one another. After passing through the coating chamber, the substrates are quickly passed into a holding chamber and then into an exit interlock. The entire transport and coating process is generally controlled by a computer.

An in-line system for sputtering Cr onto glass for the manufacture of first surface mirrors was built by the Temescal Division of Airco, Inc. It will handle substrates 0.6 m (24 inches) wide by 2.4 m (96 inches) long with a production capacity of 93,000 $m^2$ (1 million $ft^2$) per year for single shift operation. A 200 foot long glass coating line was built and is operated by Airco Temescal for Guardian Industries in Carleton, Michigan. The system will coat glass plates 2 m (80 inches) wide and up to 3.5 m (136 inches) long. The glass is placed on a conveyor belt which passes it through a washer-scrubber, through an air knife dryer, and then through a sputter coating line of the type shown in Fig. 2. The coating chamber contains six planar magnetrons which are mounted above the horizontal glass plates. Coatings are combinations of metals and dielectrics with up to four layers. The dielectric layers are deposited by reactive sputtering. Thus the basic nature of the coatings (multilayer metals and dielectrics) is identical to that required for selective surfaces. The line speed is in the 50 mm/s (10 ft/min) range. Sputtering cathode currents are greater than 200 A. The production volume for three-shift operation is greater than 930,000 $m^2$ (10 million $ft^2$) per year.

A similar machine is in operation at Shatterproof Glass, Inc., in Detroit to deposit thin metal coatings onto 1.8 m (72 inches) wide by 3.7 m (144 inches) long plates of architectural glass.

Advanced Coating Technology, Inc. built and operates a large architectural glass coating facility in Franklin, Tennessee. The glass plates are 2 m (80 inches) wide by 3.5 m (140 inches) long. The interlock scheme is the same as that shown in Fig. 2. However, in this machine the glass plates are mounted vertically and pass on each side of planar magnetron sources which are mounted back-to-back. Metal and nitride coatings are deposited. The nitride coatings are deposited reactively. Deposition rates are in the 6 to 10 nm/s (4000 to 6000 Å/min) range. Line speeds are in the 50 to 300 mm/s (10 to 60 ft/min) range. The production volume for three shifts is greater than 930,000 $m^2$ (10 million $ft^2$) per year.

Advanced Coating Technology will be placing another plant into operation in Venezuela this year. It is of the same basic design as the one described above, expect that three rather than five chambers are used. The glass is inserted and withdrawn from the same end. The production capacity is about 560,000 $m^2$ (6 million $ft^2$) per year on a three shift basis.

A number of other large production facilities are either under construction or in the planning stage. Donnelly Mirrors, Inc. in Holland, Michigan, is presently producing over a million $ft^2$ per year of metal/metal-oxide coated glass using interlock systems with planar magnetron sources and an additional sputtering system is planned. A large system in Europe will coat glass plates 2.5 m (100 inches) wide by 4.6 m (180 inches) long. Another system is under construction that will deposit oxide-metal-oxide coatings onto 1.8 m (72 inches) wide plastic sheet for subsequent lamination between glass plates. The apparatus contains five planar magnetron sources. Four are used to reactively deposit the oxide coatings. One is used for the metal coating. The strip speed is in the 10 mm/s (a few ft/min) range.

## V. APPLICATIONS IN MICROELECTRONICS

Application of coatings technology in microelectronics falls into three areas. One of them is a part of the microelectronic package and the others form active circuit elements.

Microcircuit elements are often mounted on a specially shaped base called a "lead-frame" by which suitable connections to the device can be made. Thermal compression bonding techniques are used to weld a fine (about .0001" dia) aluminum on gold wire from the appropriate location on the device to a terminal on the lead frame. The price of gold has forced the use of aluminum whenever possible. The lead frame material is an Fe-42%Ni alloy known as "kovar". Aluminum wire cannot be directly thermal-compression bonded onto the aluminum. Aluminum is moreover difficult to electroplate. As a result, it is evaporated onto the kovar substrate. Typically, a coil of kovar strip several thousand feet long is loaded into a vacuum evaporator, preheated to 350°C by rf heating and moved over multiple wire-fed resistance or electron beam evaporation source to deposit 150 to 200 microinches of aluminum. The strip after deposition is rewound and subsequently punched out in a stamping machine to form the lead frame. Some idea of the economics involved can be gauged from the fact that light emitting diodes selling at $0.09 each have a built-in cost for the lead frame of $0.02 [5]. These are 1974 prices.

Some of the active elements of microcircuits are thin film resistors and capacitors. Thin film resistors of tantalum, nichrome and cermets are deposited by evaporation or sputtering techniques followed by stablizing thermal treatments, deposition of protective coatings, laser trimming and packaging.

Thin film capacitor materials are dielectrics such as silicon monoxide, silicon dioxide, tantalum oxide, silicon nitride, etc. These films are deposited by evaporation, sputtering, CVD, and in some cases such as SiO, they are formed by thermal oxidation.

In addition to the above, evaporation and sputtering are used to form contacts for example between nichrome resistors and aluminum conductors. The problem of forming suitable contacts is one of the chief stumbling blocks in the use of new materials in devices.

Photolithography requires the use of metal film masks. These are formed from glass plates with a thin layer of chromium deposited by magnetron sputtering, r.f. sputtering or evaporation. One of the very salient features of such coatings are uniformity in thickness and impurity content and freedom from pinhole defects.

## VI. CORROSION OF AIRCRAFT PARTS

High strength steel, titanium, and aluminum alloy aircraft components are coated with aluminum on a commercial scale by ion plating methods [6-8] for corrosion protection, replacing electroplated and evaporated cadmium coatings. There are various reasons for

the use of ion plated aluminum.

1) In contrast to vacuum deposited cadmium, aluminum coating has a higher use temperature, 496°C, as compared to 232°C for cadmium.

2) It replaces diffused nickel-cadmium coatings and provides better corrosion protection at all strength levels. Diffused nickel-cadmium is limited to steels having strength levels below 200,000 psi because of hydrogen embrittlement.

3) It does not cause hydrogen embrittlement of high strength steel unlike electroplated cadmium.

4) It does not cause solid state embrittlement of titanium as in the case with cadmium.

5) It can be used in contact with fuel where cadmium use is prohibited.

6) Provides galvanic protection to aluminum alloys since it is sacrificed with respect to aluminum. It is less expensive to replace a fastner than an aluminum panel.

7) It does not cause a reduction in fatigue behaviour. Anodized coatings provide only barrier coating protection and cause reduction in fatigue life.

8) It can be applied thinner than alclad on aluminum alloys resulting in weight savings and is not limited to rolled forms as is alclad.

Figure 4 shows a schematic of an ion vapor deposition system as used at McDonnell-Douglas Corp. The parts to be coated are attached to the substrate holder for large sized components. Smaller items such as fasteners can be put into a barrel and rotated. The deposition rate is approximately 0.0001 inch per minute or 2.5 μm per minute.

Economics of the coating system can be divided into three categories - labor, materials, and utilities. Labor is the dominant cost item and each system uses one man for operation. Materials and utilities run between $5 and $15 per hour as of 1977.

The plating capacity of a 4 ft × 6 ft barrel coater is approximately 120 pounds of fastners per hour.

In another application, in the USSR, Ni is deposited by electron beam evaporation in a semicontinuous way onto perforated iron strip for use as electrodes in Ni-Cd batteries. The motivation is purely conservation of nickel.

The razor blade coated with Pt or $Cr_3Pt$ by sputtering provides corrosion protection thereby prolonging the sharpness of the edge.

## VII. HIGH TEMPERATURE CORROSION

Blades and vanes used in the hot-end of a gas turbine are subject to high stresses in a highly corrosive environment of oxygen, sulphur and chlorine containing gases. A single or monolithic material such as a high temperature alloy is incapable of providing both functions. The solution is to design the bulk alloy for its mechanical properties and provide the corrosion resistance by means of an overlay coating of an M-Cr-Al-Y alloy where M stands for Ni, Co, Fe or Ni+Co. The coating is deposited in production by electron beam evaporation and in the laboratory by sputtering or plasma spraying. These overlay coatings have several advantages over diffusion aluminide coatings. The latter lose their effectiveness at higher temperatures due to interactions with the substrate material. The composition and properties of overlay coatings can be more easily tailored to the needs of specific applications. With the potential future use of synthetic fuels, considerable research will have to be undertaken to modify such coating compositions for the different corrosion environments as well as against erosion from the particulate matter in those fuels.

A more detailed discussion has been given in the lecture of Professor D. H. Boone in this series.

## VIII. TRIBOLOGICAL APPLICATIONS (FRICTION AND WEAR)

There are two types of coatings used for tribological applications (friction, wear, lubrication). They are:

1) Soft solid film lubricants such as Au, Ag, $MoS_2$, PTFE. These films in the thickness range (2000-6000 Å) have been deposited by sputtering [9] and ion plating onto sliding and rotating bearing surfaces to reduce wear, lower the coefficient of sliding friction and increase the endurance life of these components. These sputtered lubricant films are of great importance where tolerances are close, reliability requirements are high and wear minimization by wear debris is critical. For thin (< 2000 Å) $MoS_2$ films, the coefficient of friction is 0.04. It is interesting to note that the amorphous deposit shows a high coefficient of friction and has no lubricating properties whereas a crystalline $MoS_2$ deposit produced at a higher substrate temperature shows a low coefficient of friction and good lubricating properties. Such dry-film lubricants are especially important for critical parts used in long lifetime applications since conventional organic fluid lubricants are highly susceptible to irreversible degradation over a long time.

Sputtered PTFE Films display excellent adherence and uniformity and are pore free not only on metal substrates but on glass, wood and paper substrates. The coefficients of friction depend on load, sliding speed and film thickness and vary from 0.08 to .2. Sputtered PTFE films have been applied to surgical needles for cataract operations where they have to function as a lubricant during insertion and removal.

Video discs are being sputtered with a thin layer of a solid lubricant film to protect the sound fidelity of the record.

2) Hard refractory compound films such as carbides, nitrides, borides, silicides. These films can be deposited by Activated Reactive Evaporation, Direct Evaporation, Reactive Ion Plating and Sputtering. These are hard and brittle films. They show excellent wear resistance in adhesive, abrasive, and erosive wear conditions. In contrast to ion implantation, the wear properties are not dependent on organic lubricants, i.e. these films show low wear when run dry [10]. Ion implanted surfaces will show a high wear when run dry. Some of the refractory compounds show a fairly low coefficient of friction (as low as 0.2 to 0.3). They are undoubtedly the approach when wear resistance is needed at temperatures greater than those where $MoS_2$ is stable.

## IX. COATINGS FOR CUTTING TOOLS

Cutting tools are made of high speed steel or cemented carbides. They are subject to degradation by abrasive wear as well as by adhesive wear. In the latter mode, the high temperatures and forces at the tool tip promotes micro-welding between the steel chip from the workpiece and the metal in the high speed steel tool or the cobalt binder phase in the cemented carbide. The subsequent chip breaks the microweld and causes tool surface cratering and wear. A thin layer of a refractory compound such as TiC, TiN, $Al_2O_3$ prevents the micro-welding since metal-to-metal contact is avoided. Improvements in tool life by factors of 300 to 800% are possible as well as reductions in cutting forces. The coatings are deposited by PVD and CVD techniques. The latter technique is routinely used in industry to coat carbide tool tips. The temperatures necessary for CVD processes (~ 1000°C) will temper and soften high speed steel and will produce distortion in shaped tools.

The current status is as follows:

Carbide Cutting Tools: TiC, TiN, $Al_2O_3$, HfN coatings produce improvement by a factor of 2 to 8 over uncoated tools in continuous cutting only, e.g. on coated inserts CVD and PVD processes produce equal results. In interrupted cutting, practically no improvement is evident except in two cases: 1) sputtered TiN; and 2) ARE process TiC, HfN. No data is reported on shaped tools.

High Speed Steel Tools: TiC, TiN, HfN coatings produce improvement by a factor of 2 to 8 in continuous cutting on steel and titanium as evaluated by coated inserts. CVD and PVD processes produce equal results.

Table I below shows the results reported in the literature on shaped high speed steel tools with hard coatings deposited by PVD techniques. These are entering the industrial market in Japan and USSR and may be expected to have a significant impact in USA and Europe in the future.

TABLE I
Improvements in Tool Life with Coated High Speed Steel Cutting Tools

Shaped Tools

| TOOL | COATING | IMPROVEMENT FACTOR |
|---|---|---|
| Tap | TiC | 5 to 10 (Japan) |
| End-Mill | TiN | 3 to 8 (Japan) |
| Milling Cutter | TiN | 3 (Japan) |
| Hob | TiN | 2 to 3 (Japan) |
| Gear Cutter | TiN | 2 (Japan) |
| Drill | TiN | 4 to 8 (Japan) |
| Boring Cutter | TiN | 4 to 10 (Japan) |
| Drill | TiN, MoN or $Mo_2N$ | 2 (USSR) |
| Punches | TiN, MoN or $Mo_2N$ | 3 (USSR) |
| Broaches | TiN, MoN or $Mo_2N$ | 1.7 (USSR) |

## XI. OPTICAL COATINGS AND TRANSPARENT CONDUCTING COATING

The production of reflecting surfaces for lamp reflectors by deposition of aluminum onto laquered steel and plastic substrates has been reliably carried out in production for many years. The production of reflecting telescope mirrors is another example. Coatings of other materials such as $MgF_2$, $SiO_x$, etc. is being routinely practiced by electron beam evaporation. Multilayer optical coatings with precise thickness control have come of age in the past few years with the advent of the optical thin film monitoring devices.

More recently, the need for hard transparent coatings has arisen to protect the soft metallic reflecting surfaces. Films of quartz, alumina, glass, indium-tin oxide are now being deposited by sputtering and evaporation techniques.

Indium oxide, tin oxide and indium-tin oxide are examples of transparent conducting films which are being deposited for liquid crystal display (LCD) applications. These films can be deposited by evaporation, ion plating and sputtering. The choice of the deposition technique and the deposition temperature and the post-deposition heat treatment strongly influence the electrical conductivity and optical properties.

## XII. MATERIALS CONSERVATION

The average world demand for tin plate increases steadily year by year. However, the deposits of tin are very limited and it will remain an indispensible material in many industrial applications. Since 50% of the extracted tin is used in the manufacture of tin plate, it is lost in the international economy for all time. Therefore, it is important to replace tin plate with steel strip coated by other techniques.

The initial attempts were made in the 1963 to 1966 era to produce aluminum coated steel strips, but for various technological, physical and commercial reasons, the work was abandoned in many cases.

The pilot plant demonstration of zinc deposition, 0.0006" thickness, onto steel strip 12 inches wide at a line spped of 100 ft per minute was demonstrated in 1970 [11].

In 1974, Schiller and coworkers [12] reported on the industrial electron beam evaporation coating of steel strip 400 mm wide. The schematic diagram of the process is shown in Fig. 5. The aluminum thickness is 3 μm on each side and the line speed is 3 meters per second. The power level is 250 KW for each side. The authors are confident that existing technology will permit the scale-up to wider strip (1000mm wide) and

and greater thickness.

XIII. PRODUCTION OF SELF SUPPORTED SHAPES

Vapor deposition techniques can be used to produce self supported shapes like sheet, foil, tubing. Deposits are made on substrates which are subsequently dissolved away or separated from the deposit.

In the latter case, a parting compound from the deposit should be deposited onto the substrate in a prior operation. The justification for production of such self-supoorted shapes can be considered as follows. If the deposited metal or alloy is brittle or difficult to mechanically deform, then it may be more expedient to form the shape directly by deposition. For example, Ti-6Al-4V alloy foil 12" wide at a thickness of 0.002" and in lengths of 1200 ft was deposited at the rate of 2-3 ft per minute in a pilot plant operation for the "SST" program [13]. The reason is that the alloy work hardens very rapidly and it needs a large number of roll/anneal cycles to reduce it to the thin gage required. The stated cost in 1969 for the deposited material was 1/5th of the cost of the rolled material. Hughes [13] states that limitations for such sheet or foil production are few except for foils 0.010" thickness or greater which can be produced more economically by standard rolling techniques. It should be said that there are no vapor deposition foil making plants in operation currently since it is a new technique and has to compete with installed large foil-rolling facilities.

At the other end of the scale, very thin pin-hole free foils ( 1 μm in thickness) of titanium, 2-12 cm diameter have been successfully produced [14]. In this case, or in the case of brittle materials, there is no question that vapor deposition is a very viable technique. Such foils can be used as membranes, beam strippers in large accelerators, etc.

XIV. POTENTIAL APPLICATIONS

The following lists some potential applications, many of which have been demonstrated on a laboratory scale.

1. New alloys using:
   a) very fine grain size to obtain high strength with high toughness,
   b) very fine particle sizes and spacings to produce dispersion strengthened alloys,
   c) very closely spaced and very thin single and multilaminate structures to produce high strength, high toughness composites.
2. Coatings for:
   a) corrosion resistance, e.g. a thin coating of Ti or a Ti alloy on a lower priced material as compared to fabrication of the entire item from bulk titanium,
   b) abrasion resistance on common steel and alloys using deposits of oxides, nitrides, carbides, cermets, or graded deposits,
   c) increasing tool performance of high speed steel and carbide tools,
   d) catalysis using the ability to produce very high surface areas and non-equilibrium alloys.
3. Production of ultrafine powders (<1 μm dia) of metals, alloys, ceramics, or mixtures thereof produced by evaporation and condensation in high pressure gas [15,16] or on cold surfaces [17]. Such ultrafine particles have been used in the manufacture of magnetic tapes of higher memory density and coercive force. These powders would have great utility in the production of tool steels, cermets, dispersion strengthened alloys, etc.
4. Production of new superhard materials, e.g. alloy carbides, rare-earth borides, boron nitride, etc.
5. New superconducting materials, in useful forms such as wires and tapes.
6. Development of new optical and electrical materials, e.g. compounds of controlled stoichiometry.
7. Biomedical materials, e.g. controlled porosity surfaces for implants, coaxial neurological electrodes, etc.
8. Amorphous materials and finely dispersed alloys of immiscible components.
9. TiC coatings on insulators for the manufacture of precision resistors and variable resistors in place of Ni-Cr or Pt wire wound resistors, taking advantage of the wear resistance of TiC.
10. Coating of Ti on steel wires for marine environment use.
11. Coating of steel wire with Cu followed by Ag for electrical uses. It is superior to electroplating because of reduced porosity.
12. Rhodium coating on magnetic material contacts for longer life.
13. Coating of ceramics with metals to permit easier joining by soldering or brazing subsequently.

XV. ECONOMICS AND PERSPECTIVE

In many potential applications, the unique ability of PVD techniques makes the economics a go-no-go situation, i.e. the market place will have to bear the cost of making the desired component which is otherwise impossible to fabricate. Good examples are the coated turbine blades and aircraft parts. In other situations, PVD is but one step in the manufacture of a part and the cost comparisons are hidden in systems costs. Nevertheless, some idea of economics can be obtained. For example:

1) Thornton [18] quotes the sputter coating of a particular cylindrical machined part with 0.1 mil of refractory metal at a rate of 10,000 parts per day for a single machine would cost 10-25 cents per part.

2) For difficult to roll materials, the cost of fabricating these foils (<10 mils) is expected to be significantly cheaper than producing the same foil by rolling, one factor being the high yield of the process.

3) In view of the current interest in solar energy, some estimates have been made in 1974 for semicontinuous deposition of compounds such as CdS, CdTe, etc. They are:

a) Using vacuum evaporation, it is estimated that an apparatus costing $2.4 million could produce a continuous deposit of CdS 4 ft. wide and 15 μm thick at a rate of 1 ft/sec. at a cost of $1 per square foot [19]. Another independent estimate comes up with a very similar figure [20].

b) Using high rate sputtering technology, p-CdTe/n-CdS deposits can be manufactured from a system costing $300,000 at a rate of 288 panel of each 1 sq. foot in area per day and a few microns thick at a cost of $4.40 per square foot [21].

The following statements were made by this author [22] in 1974:

> "Looking into the crystal ball, it is not difficult to see that materials requirements for the energy related applications (superconductors, high-temperature coal conversion, nuclear reactor materials), for higher productivity in machining and forming, for longer life of components (improved corrosion and wear resistance) etc. are spurring the development of coating technologies at a rapid tempo".

They are even truer today. It should be noted that PVD techniques are not just laboratory tools. They have also been demonstrated in large scale applications. Therefore, the translation from laboratory to industrial practice can be rapidly achieved. The critical step is the product development work in the laboratory. The versatility of PVD technology assures its rapid development and applications in the next decade.

REFERENCES


1. H.R. Smith, Proc. 22nd Annual Conference, Soc. Vac. Coaters, 1979, New Orleans, Louisiana, published by the Society of Vacuum Coaters, USA.
2. A.D. Grubb, J. Vac. Sci. Tech. 10: 53 (1973).
3. A.D. Grubb, J. Vac. Sci. Tech. 7: 220 (1970).
4. J.A. Thornton, "Sputter Deposited Selective Absorber Coatings," presented at the Second American Electroplaters Society, Inc., Coatings for Solar Collectors Symposium, St. Louis, Missouri, October 16-17, 1979.
5. H.R. Smith, Jr., "A Continuous System for Lead Frame Coating," Proceedings 17th Annual Conference, Soc. Vac. Coaters, 1974, published by the Society of Vacuum Coaters, USA.
6. L.E. McCrary, J.F. Carpenter and A.A. Klein, in Trans. Vac. Met. Conf., 1968, published by American Vacuum Society, pg. 221.
7. K.E. Steube and L.E. McCrary, J. Vac. Sci. Tech. 11: 362 (1974).
8. E.R. Fannin, "Ion Vapor Deposited Aluminum Coatings," McAIR No. 77-014, McDonnell Aircraft Co., St. Louis, Missouri, 1977.
9. T. Spalvins, "Sputtering Technology in Solid Film Lubrication," Proc. 2nd Int. Conf. on Solid Lubrication, Am. Soc. of Lubrication Engineers, 1978, pg. 109-117.
10. A.K. Suri, R. Nimmagadda and R.F. Bunshah, Thin Solid Films, 64:191(1979).
11. J.F. Butler, J. Vac. Sci. Tech. 7: S52 (1970).
12. S. Schiller, P. Lenk, H. Foerster, G. Jaesche and G. Kuehn, Third Electron Beam Processing Seminar, Stratford-upon-Avon, England, March 1974, published by University Technology Corporation, Dayton, Ohio.
13. J.L. Hughes, Metals Eng. Quarterly 14: 1 (1974).
14. V.Y. Pickhardt and D.L. Smith, J. Vac. Sci. Tech. 14: 823 (1977).
15. P.J. Clough, in New Types of Metal Powders, Gordon and Breach, 1964, p. 9.
16. C. Hayashi, Japanese J. of Appl. Phys. 12: 1675 (1973).
17. R.F. Bunshah, unpublished research.
18. J.A. Thornton, "Designing the Surface for the Job-Thin Film Applications," 19th National SAMPE Symposium, Buena Park, CA, April 23-25, 1974.
19. K.W. Boer, Annual Progress Report NSF/RANN/SE/GI-34872, University of Delaware, January 1974.
20. T.P. Brody and F.A. Shirland, Proc. NSF Workshop on Photovoltaic Conversion of Solar Energy for Terrestrial Applications, Cherry Hill, NJ, October 1973, p. 168.
21. N. Laegreid, ibid, p. 63.
22. R.F. Bunshah, "Physical Vapor Deposition of Metals, Alloys and Ceramics," published in New Trends in Materials Processing, American Society for Metals, 1974.

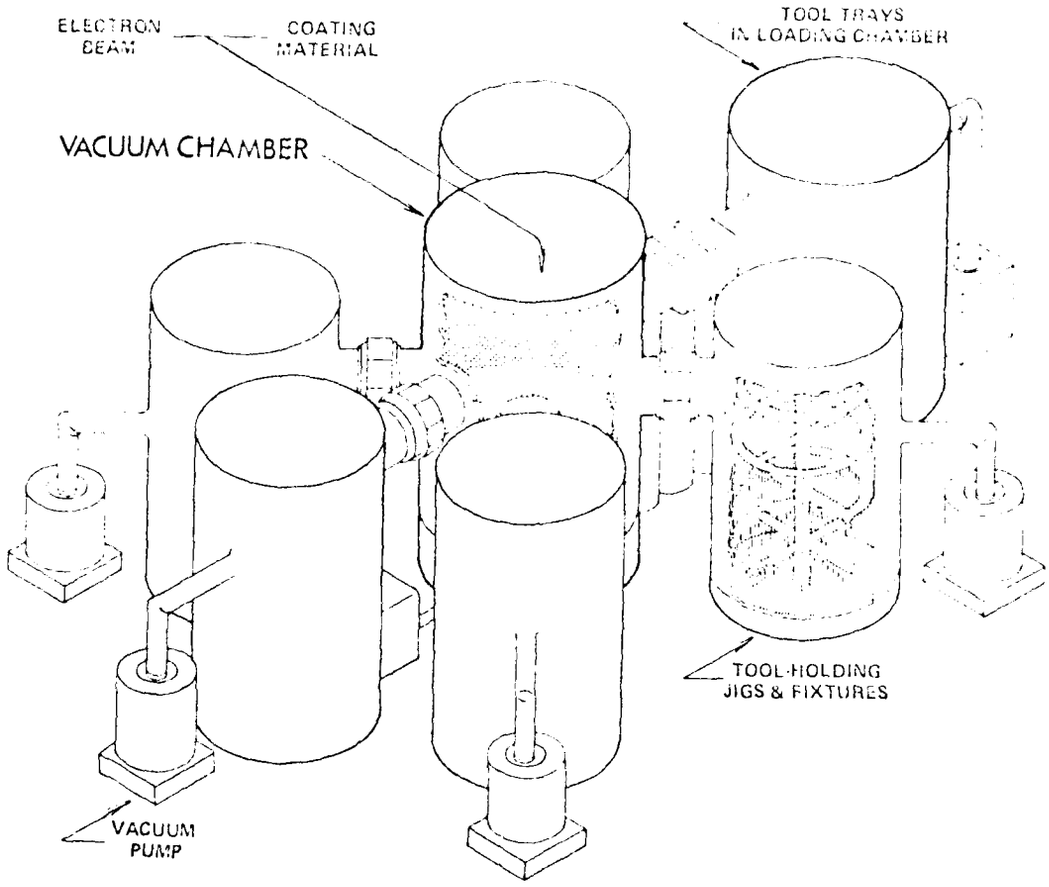


FIGURE 1. Schematic (conceptual) of a fast-cycle tool coating apparatus.

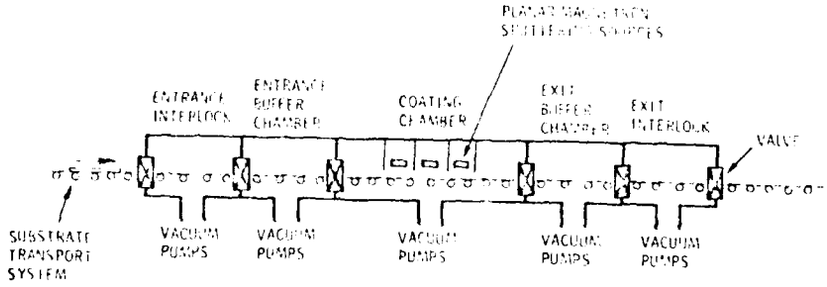


FIGURE 2. Schematic representation of in-line coating system of the type that is used to deposit sputtered coatings on architectural glass plates and that could be used for depositing selective absorber coatings on flat plate collector panels. (Thornton [4]).

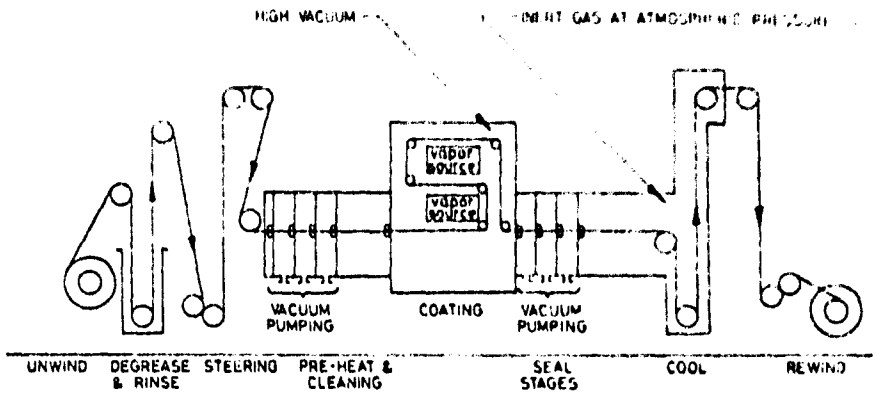


FIGURE 3. Schematic of a continuous arc-to-vacuum-to-air electron beam coating line.

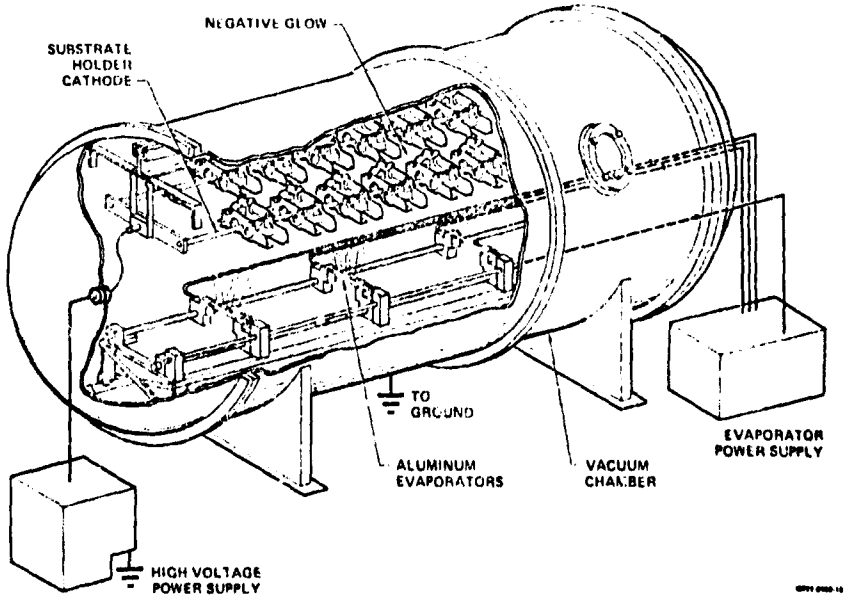


FIGURE 4. Schematic of an ion-plating deposition system. (Fannin [4]).

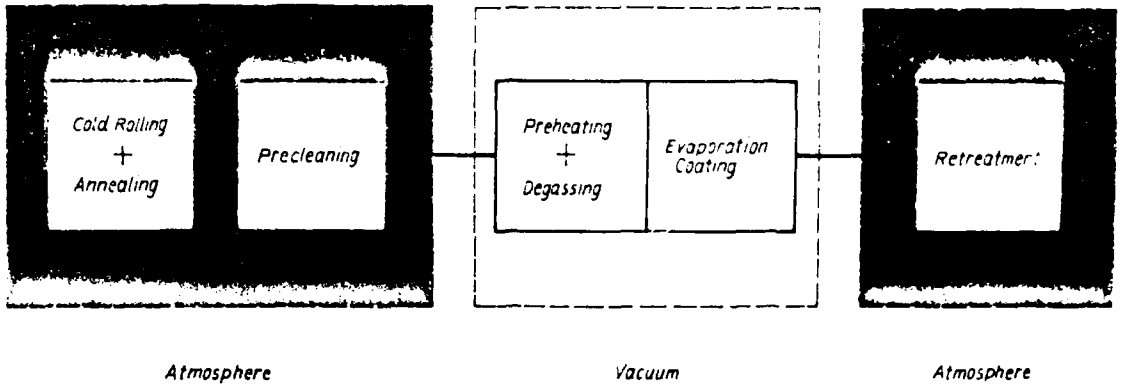


FIGURE 5. Processing steps in a steel strip finishing line for evaporation coating. (Schiller et al [12]).

# BIBLIOGRAPHY ON COATING PROCESSES

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# SELECTIVE BIBLIOGRAPHY

The Bibliography which follows is a compilation of report references selected to suit this particular Lecture Series; it is not intended to be comprehensive. The references are presented in reverse chronological order, according to the date of publication of the report, in each section.

It is regretted that AGARD cannot undertake to provide copies of the documents listed. These should be sought through National Library Centres or from the organisations which published them.

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ION BEAM SPUTTER ETCHING AND DEPOSITION OF FLUOROPOLYMERS
Banks, B. A.; Sovey, J. S.; Miller. T. B.; Crandall, K. S.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-78888, 1978, 17p, Monitor: 18, Conf-Presented at the 8th Intern. Conf. On Electron and Ion Beam Sci. and Tech., Seattle, 21-26 May 1978; Sponsored by the Electrochemical Soc., Inc.

2 N78-28100 NASA Issue 19 Category 7
THE PROTECTIVE COATING BY ION PLATING OF TURBINE BLADES
Battelle Memorial Inst., Geneva (Switzerland). (BE209669) 760421 4 p. Jpn. 2487
HC A02/MF A01

3 LA-UR-77-1261
CHEMICAL VAPOR DEPOSITION OF TANTALUM ON GRAPHITE CLOTH FOR MAKING HOT PRESSED FIBER REINFORCED CARBIDE-GRAPHITE COMPOSITE
Hollabaugh, C. M.; Davidson, K. V.; Radosevich, C. L.; Riley, R. E.; Wallace, T. C.
Los Alamos Scientific Lab., N.Mex.*Energy Research and Development Administration (3820000)
Rept No: CONF-771004-1, 1977, 18p, Contract: W-7405-ENG-36, Monitor: 18, International conference on chemical vapor deposition, Atlanta, Georgia, USA, 10 Oct 1977.

4 N77-27214/4SL
THEORETICAL AND EXPERIMENTAL STUDIES OF THE DEPOSITION OF NA2SO4 FROM SEEDED COMBUSTION GASES
Kohl, F. J.; Santoro, G. J.; Stearns, C. A.; Fryburg, G. C.; Rosner, D. E.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-X-73683, E-9031, 13 May 77, 29p, Monitor: 18, Conf-Presented at the Symp. On Corrosion Probl. Involving Volatile Corrosion Prod., Philadelphia, 8-13 May 1977; Sponsored by the Electrochemical Society.

5 AD-A046 000/6SL
GRADED PYROLYTIC GRAPHITE/SILICON CARBIDE COATING DEPOSITION STUDIES
Copeland, Joseph P.; Undercoffer, Kenneth E.
Atlantic Research Corp Alexandria Va (045550)
Final rept. Jul 74-Oct 75, Apr 77, 153p, Contract: F33615-74-C-5103, Project: 7340, Task: 01, Monitor: AFML-TR-76-122.

6 AD-A044 618/7SL
A PLASMA FLAME SPRAY HANDBOOK
Roseberry, T. J.; Boulger, F. W.
Battelle Columbus Labs Ohio (407080)
Final rept, Mar 77, 161p, Contract: N00197-73-C-4030, Monitor: NAVSEA-MT-043, Report on Manufacturing Technology Program.

7 N77-15097/7SL
SUMMARY OF NASA RESEARCH ON THERMAL-BARRIER COATINGS
Stepka, F. S.; Liebert, C. H.; Stecura, S.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Report No: NASA-TM-X-73584, 1977, 27p, Monitor: 18, Conf-Proposed for Presentation at the Automotive Eng. Conf., Detroit, 28 Feb.-4 Mar. 1977; Sponsored by the SAE.

8 N77-21241/3SL
PLASMA SPRAYED SOLID LUBRICANT FILMS FOR OIL- AND GREASEFREE BEARINGS. STUDIES OF CHALCOGENIDE FILMS AND TESTING OF SLIDE COUPLES UNDER NORMAL CONDITIONS AND IN VACUUM
Kirner, K.
Bosch (Robert) G.m.b.H., Gerlingen (West Germany)
Final Report, Rept No: BMFT-FB-W-76-16, Nov 76, 101p, Contract: BMFT-RFT-3772, GFW-RV-11-TB-4/72-Z, Monitor: 18, In German; English Summary.

9 GA-A-13845
STRUCTURE OF CHEMICAL VAPOR DEPOSITED SILICON CARBIDE
Chin, J.; Gantzel, P. K.; Hudson, R. G.
General Atomic Co., San Diego, Calif.*Energy Research and Development Administration (9500489)
Rept No: CONF-760454-1, 15 Mar 76, 32p, Contract: E(04-3)-167, Monitor: 18, American Vacuum Society Conference, San Francisco, California, United States of America (USA), 5 Apr 1976.

10 AD-A032 554/8SL
CONTROLLED COMPOSITION REACTION SINTERING PROCESS FOR PRODUCTION OF CoCrAlY COATINGS
Stevens, W. G.; Stetson, A. R.
Solar San Diego Calif (326550)
Final Rept. 11 Jul-15 Dec 75, Rept No: RDR-1802-6, Aug 76, 60p, Contract: F33615-75-C-5268, Project: 7312, Task: 01, Monitor: AFML-TR-76-91.

11 N77-13966 NASA Issue 4 Category 26
THERMOCHEMICAL DEPOSITS ON TITANIUM ALLOYS
Lepetit, P.; Hivert, A.
European Space Agency, Paris (France). (E6854803)
761100 In its La Rech. Aerospatiale, Bi-monthly Bull. No. 1971-1 (ESA-TT-351) p 60-73 (SEE N77-13962 04-99) Transl. into ENGLISH from La Rech. Aerospatiale, Bull. Bimestriel (Paris), no. 1976-1, Jan.-Feb. 1976 p 37-44 Original report in FRENCH previously announced as A76-28754 14p. Jpn. 549

12 GA-A-13254
PREPARATION OF SILICON NITRIDE COATINGS BY ION PLATING
Chin, J.; Elsner, N. B.
General Atomic Co., San Diego, Calif (9500489)
Rept No: CONF-750234-1, 9 Dec 75, 25p, Contract: AT(04-3)-943, Monitor: 18.

13 AD-A024 109/1SL
THE SPUTTER DEPOSITION AND EVALUATION OF TUNGSTEN AND CHROMIUM FOR USE IN WEAPON COMPONENTS
Jones, R. H.; Moss, R. W.; McClanahan, E. D.; Butts, H. L.
Battelle Memorial Inst Richland Wash Pacific Northwest Labs (387060)
Technical rept, Oct 75, 47p, Project: PRON-M1-4-A1555-01-M1-MS, Monitor: RIA-R-TR-75-042.

14 GA-A-13432
PREPARATION OF SILICON--ALUMINUM NITROGEN COMPOUNDS E REACTIVE ION PLATING
Chin, J.; Elsner, N. B.
General Atomic Co., San Diego, Calif (9500489)
Rept No: CONF-750922-1, 23 Apr 75, 18p, Monitor: 18, NTIS

15 N76-16448 NASA Issue 07 Category 37
PREPARATION OF SILICON NITRIDE COATINGS BY ION PLATING
Chin, J.; Elsner, N. B.
Gulf General Atomic, San Diego, Calif. (G9153964)
GA-A-13254 CONF-750234-1 091275 AT(04-3)-943 Presented at the Conf. on Structure-Property Relationship in Thick Film Bulk Coatings, San Francisco, 10-12 Feb. 1975 25 p. Jpn 854 HC

16 AD-A018 130/5SL
THE FORMATION OF REFRACTORY METAL ALLOYS BY SIMULTANEOUS DEPOSITION OF METALS FROM THE GASEOUS PHASE
Crowson, Andrew
Rock Island Arsenal Ill General Thomas J Rodman Lab (408247)
Technical rept. Sep 73-Jun 74, Rept no: RIA-R-TR-74-047, Jul 74, 36p, Project: DA-1-T-162105-AH-84, Monitor: 18, NTIS

17 N75-14149/9SL
LUBRICATION OF BALL BEARINGS UNDER VACUUM LUBRIFICATION SOUS VIDE DE ROULEMENTS A BILLES
Gass, H.; Hintermann, H. E.; Kocher, H. R.
Laboratoire Suisse de Recherches Horlogeres, Neuchatel (Switzerland) Interim Report, Rept No: ESRO-CR-163, Jan 74, 45 p, Contract: ESTEC-1495/71-HP, Monitor: 18, Language in French.

18 AD-917 984/7SL
PROCESS DEVELOPMENT AND CHARACTERIZATION OF CHEMICAL VAPOR DEPOSITED TUNGSTEN FOR GUN BARREL APPLICATIONS
Harlow, Richard A.; Corn, David L.
Philco-Ford Corp Newport Beach Calif Aeronutronic Div (401 965)
Final Rept. Dec 71-Sep 73, Oct 73, 69p, Contract: F08635-72-C-0106, Project: AF-670A, Task: 2, Monitor: AFATL-TR-73-205, Distribution limitation now removed.

19 N75-28132 NASA Issue 19 Category 24
POTENTIAL APPLICATIONS OF THE CHEMICAL VAPOUR DEPOSITION PROCESS IN THE DEVELOPMENT OF COMPOSITES
Poeschel, E.
British Library Lending Div., Boston Spa (England). (BZ232127) BLL-BTI-0746-01493-(9022.401) 00117 Transl. into ENGLISH from Z. Werkstofftech. (West Germany), No. 4, 1973 p 215-221 in ENGLISH and GERMAN Jpn. 2356 Avail: British Library Lending Div., Boston Spa, Engl.: 2 BLL Photocopy coupons

20 N73-16523 NASA Issue 07 Category 15
INFLUENCE OF VARIOUS SURFACE PRETREATMENTS ON ADHERENCE OF SPUTTERED MOLYBDENUM DISULFIDE TO SILVER, GOLD, COPPER, AND BRONZE (INFLUENCE OF SURFACE FINISHING ON ADHERENCE OF RADIO FREQUENCY SPUTTERED MOLYBDENUM DISULFIDE ON SILVER, GOLD, COPPER, AND BRONZE)
Spalvins, T.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio. (ND315753)
NASA-TN-D-7169 E-7062 000273 19 p. Washington Jpn. 804 HC

21 UCSD-34P162-4
NEW MATERIALS BY LOW TEMPERATURE CONDENSATION. PROGRESS REPORT
Luo, H. L.
California Univ., San Diego, La Jolla.*Energy Research and Development Administration (1138000) 1 Sep 72, 14p, Contract: AT(04-3)-34, Monitor: 18, NTIS

22 AD-750 517
PLASMA BABBITT SURFACING OF THE STEEL BASE OF BEARINGS
Bruk, M. V.; Khmelevskaya, V. B.
Foreign Technology Div Wright-Patterson AFB Ohio (141600)
Rept No: FTD-HC-23-0882-72, 25 Aug 72, 8p, Project: AF-7343, Monitor: 18, Unedited rough draft trans. of Institut Vodnogo Transporta, Leningrad. Trudy (USSR) n126 p49-52 1971.

23 N72-28502
PROCESS FOR PRODUCING NICKEL ALUMINIDE COATING LOW ALLOY STAINLESS STEEL
Grisaffe, S. J.; Klechka, E. W.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Patent Application, Rept No: NASA-CASE-LEW-11267-2, pat-appl-273223 Filed 19 Jul 72, 12p, Monitor: 18, Government-owned invention available for licensing. Copy of application available NTIS,

24 AD-751 203
LOW TEMPERATURE METAL OXIDE DEPOSITION BY ALKOXIDE HYDROLYSIS
Sladek, Karl J.; Gibert, W. Wayne
Texas Univ Austin Electronics Research Center (403789) 1972, 20p, Contract: F44620-71-C-0091, Project: AF-4751, Monitor: AFOSR-TR-72-2091, Availability: Pub. in Proceedings of the International Conference on Chemical Vapor Deposition (3rd), Salt Lake City, Utah, 24-27 Apr 72 p215-231 1972.

25 AD-742 821
I. NEW TECHNIQUES FOR THE SYNTHESIS OF METALS AND ALLOYS. II. THE PROPERTIES OF RARE EARTH METALS AND ALLOYS
Bunshah, R. F.; Douglass, D. L.
California Univ Los Angeles School of Engineering and Applied Science (404637)
Semi-Annual technical rept. no. 3, Rept no: UCLA-ENG-7227, Mar 72 55p, Grant: DAHC15-70-G-15, See also Semi-Annual technical rept. no. 2, AD-731 375.

26 BNWL-TR-280
PRODUCTION OF THIN METAL FILMS BY CATHODE SPUTTERING
Siegle, G.
1972, 30p, Contract: EY-76-C-06-1830, Monitor: 18, Translated from Oberflaechentech./Metallprax. 21 n7 P247-254 1972,

27 N72-16439
ALLOYED COATINGS FOR DISPERSION STRENGTHENED ALLOYS
Wermuth, F. R.; Stetson, A. R.
Solar, San Diego, Calif
Rept No: NASA-CR-120852, RDR-1686-3, Oct 71, 98p, Contract: NAS3-14312, Processing Techniques for Applying Diffusion Barrier Coatings to Dispersion Strengthened Alloys, NTIS

28 AD-7[illegible] [illegible]75
I. NEW METHODS OF SYNTHESIS OF MATERIALS. II. THE PROPERTIES OF RARE EARTH METALS AND ALLOYS
Runshah, R. F.; Douglass, D. L.
California Univ Los Angeles School of Engineering and Applied Science (404637)
Semi-Annual technical rept. No. 2, 1 Mar-31 Jul 71, Rept no: UCLA-ENG-7161, 1 Sep 71, 70p,
Grant: DAHC15-70-G-15, See also Semi-Annual technical rept. no. 1, AD-722 088,

29 AD-7[illegible] 94[illegible]
INVESTIGATION OF COATING PLASTIC LENSES WITH SPUTTER-DEPOSITION PROCESS
Meckel, Ben B.; Harkins, Patrick A.
Physics Technology Labs Inc La Mesa Calif (388407)
Final rept. 14 Jan 7[illegible]-[illegible] Jun 71, Rept no: A-0094, 1 Jun 71, 33p, Contract: DAAA15-70-C-0269

30 AD-865 504
CHEMICAL VAPOR DEPOSITION (CVD) BARREL COATING FOR REFRACTORY FASTENERS
Wakefield, Gene F.; Yaws, Carl L.
Texas Instruments, Inc., Dallas (347 650)
Final technical rept. 1 Apr 68-1 Oct 69, Rept no: TI-04-69-09, Dec 69, 258p, Monitor: AFML TR-69-316, Distribution Limitation now Removed

31 N70-11711 NASA Issue 02 Category 18
STUDY OF TITANIUM CARBIDE COATINGS DEPOSITED ON A STEEL SURFACE (TITANIUM CARBIDE COATINGS DEPOSITED ON STEEL SURFACE)
Semenova, G. A.
Air Force Systems Command, Wright-Patterson AFB, Ohio. (AJ773273)
AD-693440; FTD-HT-23-1354-68 090669 Date- 9 Jun. 1969 Coll-7 P Refs Tran-TRANSL. into English from the Russian Avail - CFSTI

32 AD-848 585
IMPROVED HIGH-TEMPERATURE SOLID FILM LUBRICANTS
Hopkins, Vern; Hubbell, Ronald D.; Lavik, Melvin T.
Midwest Research Inst., Kansas City, Mo (230 350)
Technical rept. 1 Jun 67-1 Dec 68, Feb 69, 307p, Contract: AF 33(615)-5278, Project: AF-7343.
Monitor: AFML-TR-67-223-PT-2, Distribution Limitation now Removed

33 N68-17338 NASA Issue 08 Category 17
DEVELOPMENT OF PROTECTIVE COATINGS FOR CHROMIUM-BASE ALLOYS (RESISTANCE TO OXIDATION AND NITROGEN ABSORPTION DURING CYCLIC OXIDATION OF METALLIC CLADDING SYSTEMS APPLIED TO CHROMIUM BASED ALLOYS BY GAS PRESSURE BONDING)
Bartlett, E. S.; English, J. J.; Ernst, R. H.; MacMillan, C. A.; Williams, D. N.
Battelle Memorial Inst., Columbus, Ohio. (BE112895)
NASA-CR-54619 050368 NAS3-7612 Date- 5 Mar. 1968 Coll- 154p Refs CFSTI

34 AD-822 099
EXTRUDING AND DRAWING MOLYBDENUM TO COMPLEX THIN H-SECTION
Santoli, P. A.
Allegheny Ludlum Steel Corp., Brachenridge, Pa (018 360)
Final rept. 1 Jul 63-15 Jul 67, Aug 67, 183p, Contract: AF 33(657)-11203, Project: AF-8-112,
Monitor: AFML-TR-67-237, Distribution Limitation now Removed

35 N67-28796 NASA Issue 15 Category 17
THE DEVELOPMENT OF DISPERSION STRENGTHENED NICKEL-BASE CORROSION RESISTANT ALLOYS (DISPERSION-HARDENED CORROSION RESISTANT NICKEL ALLOYS BY VAPOR PLATING IN FLUIDIZED BED OF OXIDE PARTICLES)
Melpar, Inc., Falls Church, Va. (MS336198)
NASA-CR-54580 000567 NAS3-7271 May 1967 16p Refs CFSTI

36 N71-16077 NASA Issue 06 Category 15
METHOD OF COATING CARBONACEOUS BASE TO PREVENT OXIDATION DESTRUCTION AND COATED BASE PATENT (FLAME OR PLASMA SPRAYING FOR MOLYBDENUM COATING OF CARBON OR GRAPHITE SURFACES TO PREVENT OXIDATIVE CORROSION)
Jewell, R. A.; Wakelyn, N. T.
National Aeronautics and Space Administration. Langley Research Center, Langley Station, Va. (ND 210491)
NASA-CASE-XLA-00302; US-PATENT-3,271,181; US-PATENT-APPL-SN-284266 060066 DATE- Issued 6 Sep. 1966/Filed 29 May 1963/ Coll- 4p Seri-CL. 117-46 Avail- US Patent Office

37 N71-16075 NASA Issue 06 Category 15
METHOD OF COATING CARBONACEOUS BASE TO PREVENT OXIDATION DESTRUCTION AND COATED BASE PATENT (VAPOR DEPOSITED LAMINATED NITRIDE-SILICON COATING FOR CORROSION PREVENTION OF CARBONACEOUS SURFACES)
Jewell, R. A.; Wakelyn, N. T.
National Aeronautics and Space Administration. Langley Research Center, Langley Station, Va. (ND210491)
NASA-CASE-XLA-00284; US-Patent-3,264,135; US-Patent-Appl-SN-240760 020866 Date Issued 2 Aug. 1966/Filed 28 Nov. 1962/Coll- 5p SERI-CL. 117-69 Avail US Patent Office

38 N66-34865 NASA Issue 20 Category 28
INVESTIGATION OF KILOVOLT ION SPUTTERING QUARTERLY PROGRESS REPORT, MAY-JULY 1966 (ALUMINUM SPUTTERING, AND NEUTRON ACTIVATION ANALYSIS AFTER CESIUM ION BOMBARDMENT)
Hurlbut, F. C. Olson, N. T.; Pigford, T. H.; Smith, H. P., Jr.
California Univ., Berkeley. (CC747787)
NASA-CR-54908 310766 NAS3-5743 31 Jul. 1966 22p Refs ITS Ser. No. 7. Issue 31 CFSTI

39 N-65-34221 NASA Issue 22 Category 15
VAPOR-DEPOSITED THIN GOLD FILMS AS LUBRICANTS IN VACUUM 10-11 mm HG/ (VAPOR-DEPOSITED THIN GOLD FILMS AS LUBRICANT IN VACUUM)
Buckley, D. H.; Spalvins, T.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio. (ND315753)
NASA-TN-D-3040 001065 Washington, NASA, Oct. 1965 15p Refs CFSTI

40 N-65-28276 NASA Issue 17 Category 18
PLASTICS AND RUBBER SELECTED ARTICLES (THERMAL AFTERTREATMENT AND FLAME SPRAYING CHARACTERISTICS OF POLYAMIDE COATINGS)
Air Force Systems Command, Wright-Patterson AFB, Ohio. (AJ773273)
FTD-TT-64-1324/1&2; AD-463087 290465 29 Apr. 1965 25p Refs Transl. into English from Plastics und Kautschuk/Leipzig/, V. 11, No. 1, 1964 P 36-42

41 N65-17255 NASA Issue 07 Category 25
INVESTIGATION OF KILOVOLT ION SPUTTERING QUARTERLY PROGRESS REPORT (COPPER AND MOLYBDENUM CRYSTAL SPUTTERING UNDER CESIUM AND MERCURY ION BEAM BOMBARDMENT)
Hurlbut, F. C.; Smith, H. P., Jr.
California Univ., Berkeley. (CC747787)
NASA-CR-54129 310165 NAS3-5743 31 Jan. 1965 30 p Refs OTS-

42 N65-15591 NASA Issue 06 Category 17
VAPOR-DEPOSITED TUNGSTEN (CHEMICAL VAPOR DEPOSITION OF TUNGSTEN BY PYROLYSIS AND THERMOCHEMICAL REDUCTION)
General Dynamics Corp., San Diego, Calif. (GD201306)
NASA-CR-54266; GA-5640 061064 NAS3-4165 6 Oct. 1964 28p Refs OTS

43 N63-18283 NASA Issue 17 Category 17
(TECHNIQUES TO COAT BIMETAL JOINT USING METAL FLAME-SPRAY METHOD TO PREVENT GALVANIC CORROSION)
Knanishu, J.
Rock Island Arsenal Lab., Ill. (RX132180)
RIA-63-1419 010563 N63-18283 Rock Island Arsenal Lab., Ill. Galvanic Protection by Metal Spray Method Technical Report J. Knanishu May 1, 1963 47p 6 refs (RIA-63-1419) OTS-

44 N66-24970 NASA Issue 13 Category 22
TUNGSTEN CLADDING OF URANIUM-ZIRCONIUM CARBIDES BY VAPOR DEPOSITION (TUNGSTEN CLADDING OF URANIUM;ZIRCONIUM CARBIDES BY VAPOR DEPOSITION)
Lindgren, J. R.
General Dynamics Corp., San Diego, Calif. (GD201306)
NASA-CR-74685; GAMD-4220 080363 NAS3-2532 8 Mar. 1963 21p CFSTI

45 AD-248 900/3SL
SPUTTERING YIELDS
Wehner, G. K.
General Mills Inc Minneapolis Minn (150 400)
Rept No: 2136, 15 Nov 60, 88p, Contract: NONR-1589(15), Monitor: 18, Distribution limitation now removed. NOTE: Only 35mm microfilm is available. No microfiche.

B: HIGH TEMPERATURE APPLICATIONS

46 N79-11057 NASA Issue 2 Category 7
ABRASIVE COATINGS AS SELF CLEANING GAS TURBINE COMPRESSOR VANE TIP SEALS
Stetson, A. R.; Vogan, J. W.; Compton, W. A.
Solar Turbines International, San Diego, Calif. (SR[illegible])
780800 Materials Engineering Dept. in AGARD Seals Technol. in Gas Turbine Eng. 1[illegible]p
(See N79-11056 02-07) 16p. Jpn.

47 N78-31212/1SL
EFFECTS OF COMPOSITIONAL CHANGES ON THE PERFORMANCE OF A THERMAL BARRIER COATING SYSTEM
Stecura, S.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-78976, E-9751, Aug 78, 33p, Monitor: 18, Conf-Proposed for Presentation at the 3D Ann. Conf. on Composite and Advanced Mater., Merritt Island, Fla. 21-24 Jan. 1979

48 N79-12223/0SL
DEVELOPMENT OF SPRAYED CERAMIC SEAL SYSTEMS FOR TURBINE GAS PATH SEALING
Bill, R. C.; Shiembob, L. T.; Stewart, O. L.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept. No.: NASA-TM-79022, E-9819, 1978, 22p, Monitor: 18, Conf-Presented at the Winter Ann. Meeting, San Francisco, 10-15 Dec. 1978; Sponsored by AM. Soc. of Mech. Engr.

49 AD-A051 800/1SL
DEVELOPMENT OF ABRASIVE BLADE TIP COATINGS FOR USE IN AN ABRADABLE TURBINE GAS PATH SEAL SYSTEM
Wallace, Matthew, J.
Pratt and Whitney Aircraft Group West Palm Beach Fla Government Products Div (392837)
Final rept. 1 Jan-31 Dec 76, Rept No: FR-8324, Apr 77, 70p, Contract: F33615-76-C-5048, Project: 7312, Task: 01, Monitor: AFML-TR-77-47,

50 N77-22491 NASA Issue 13 Category 37
TECHNOLOGY DEVELOPMENT OF A CVD SILICON CARBIDE RADIAL TURBINE ROTOR INTERIM REPORT
Engdahl, R. E.
Deposits and Composites, Inc., Herndon, Va. (DM605264)
AD-A031595; DCI-113R-1 760318 DAAK02-74-C-0246 87p. Jpn. 1729 HC A05/MF A01

51 N77-25534/7SL
DEVELOPMENT OF A PLASMA SPRAYED CERAMIC GAS PATH SEAL FOR HIGH PRESSURE TURBINE APPLICATIONS
Shiembob, L. T.
Pratt and Whitney Aircraft, East Hartford, Conn. Commercial Products Div
Final Report, 2 Oct. 1975-31 Dec. 1976, Rept No: NASA-CR-135183, PWA-5521, 24 May 77, 124p
Contract: NAS3-19759, Monitor: 18

52 AD-A046 761/3SL
EXTEND CoCrAlY and Pt Sputter- Deposition Technology to Provide Coatings on FT4 Turbine Vanes for at-Sea Evaluation
Patten, J. W.; Moss, R. W.; Hays, D. D.; McClanahan, E. D.; Lundgren, R. A.
Battelle Pacific Northwest Labs Richland Wash (401048)
Technical report 16 Jan-31 Dec 76, 16 Dec 76, 32p Contract: N00024-75-C-4332, Monitor: 18,

53 AD-A037 349/8SL
APPLICATION OF SPUTTER-DEPOSITED LAMELLAR COMPOSITE TECHNOLOGY TO THE DEVELOPMENT OF HIGH TEMPERATURE TURBINE BLADE MATERIALS AND AIRFOIL FABRICATION
Busch, R.; Patten, J. W.; Gardner, H. R.
Battelle Pacific Northwest Labs Richland Wash (401048)
Final rept. 1 May 73-30 Jun 76, Oct 76, 37p, Contract: F44620-73-C-0071, ARPA Order-2482, Monitor: AFOSR-TR-77-0186

54 N77-15170 NASA Issue 6 Category 26
POWDER FABRICATION OF FIBRE-REINFORCED SUPERALLOY TURBINE BLADES
Mazzei, P. J.; Vandrunen, G.; Hakim, M. J.
Canadian Westinghouse Co. Ltd., Hamilton (Ontario). (CF694689) 761100 Turbine and Generator Div. in AGARD Advan. Fabric. Tech. in Powder Met. and their Econ. Implications 16p (See N77-15152 06-26) 16p Jpn. 725 HC A11/MF A01

55 FE-1765-4
HIGH TEMPERATURE GAS TURBINE ENGINE COMPONENT MATERIALS TESTING PROGRA. QUARTERLY PROGRESS REPORT NO. 1, JUNE 27-SEPTEMBER 28, 1975
Flynt, F. V.
General Electric Co., Schenectady, N.Y.*Energy Research and Development Administration (2681000)
15 Oct 75, 58p, Contract: E(49-18)-1765, Monitor: 18, NTIS

56 AD-A021 530/1SL
RESEARCH WITH IN-SITU COMPOSITES ALIGNED WITH EUTECTOID AND EUTECTIC TRANSFORMATIONS
Smeggil, J. G.
General Electric Corporate Research and Development Schenectady NY *Air Force Materials Lab., Wright-Patterson AFB, Ohio (406617)
Final rept. 1 May 73-1 May 75, Rept no: SRD-75-095, Aug 75, 153p, Contract: F33615-73-C-5083, Project: AF-7353, Task: 735306, Monitor: AFML-TR-75-133

57 AD-A020 633/4SL
LAMELLAR COMPOSITES FORMED BY SPUTTER DEPOSITION; PROPERTIES AND POTENTIAL APPLICATION TO TURBINE BLADES
Busch, R. A.; Patten, J. W.
Battelle Pacific Northwest Labs Richland Wash*Air Force Office of Scientific Research, Bolling AFB, DC.*Advanced Research Projects Agency, Arlington, Va (401048)
Annual technical rept. 1 May 74-30 Jun 75, Jul 75, 88p, Contract: F44620-73-C-0071, ARPA Order-2482-2, Project: AF-6813, AF-9782, Task: 681307, 978205, Monitor: AFOSR-TR-76-0013, See also report dated Jul 74, AD-787 875

58 AD-775 346/0
DEVELOPMENT AND EVALUATION OF PG/SiC CODEPOSITED COATINGS FOR ROCKET NOZZLE INSERTS. VOLUME 1. INSERT TEST AND EVALUATION IN HIGH PERFORMANCE PROPELLANT ENVIRONMENTS
Bielawski, Cedric; Undercoffer, Kenneth E.; Singleton, Richard H.
Atlantic Research Corp Alexandria Va (045550)
Final Rept. Apr 72-Aug 73, Rept No: 46-5544-I-2/4, 46-5544-II-1/2, Feb 74, 141p, Contract: F04611-72-C-0047, Project: AF-3148, Monitor: AFRPL-TR-73-107-VOL-1, See also Volume 2, AD-775 347, NTIS

59 AD-775 347/8
DEVELOPMENT AND EVALUATION OF PG/SiC CODEPOSITED COATINGS FOR ROCKET NOZZLE INSERTS. VOLUME II. THERMOSTRUCTURAL ANALYSES OF SELECTED NOZZLE TEST FIRINGS
Murray, James W.; Vaughan, Jeffrey R.; Anderson, Carl W. Jr
Atlantic Research Corp Alexandria Va (045550)
Final rept. Apr 72-Aug 73, Rept no: 46-5544-II-3/4, Feb 74, 397p, Contract: F04611-72-C-0047, Project: AF-3148, Monitor: AFRPL-TR-73-107-VOL-2, See also Volume 1, AD-775 346

60 AD-756 867
METAL MATRIX COMPOSITES FOR HIGH TEMPERATURE APPLICATION
Ahmad, I.; Barranco, J. M.; Heffernan, W. J.; Loomis, K. E.
Watervliet Arsenal NY (371050)
Technical rept, Rept no: WVT-7266, Dec 72, 104p*, Project: DA-1-T-0[illegible]-A-[illegible], Monitor: 18,

61 N73-23647 NASA Issue 14 Category 18
CARBON RESEARCH/SEMIANNUAL TECHNICAL REPORT, 1 Jul. - 31 Dec. 1972 (DEPOSITION PROCESS INVESTIGATION OF STEADY-STATE FLUID BEDS TO OBSERVE CARBONIZATION OF PYROLYTIC MATERIALS)
Akins, R. J.; Kaae, J. L.; Koyama, K.; Price, R. J.; Shim, H. S.
Gulf Electronic Systems, San Diego, Calif. (G9108662)
AD-757118 GULF-EL-A12500 [illegible]0173 DAHC15-71-C-0282 ARPA ORDER 1861 50p Jpn. 1682

62 N71-11635 NASA Issue 02 Category 18
TECHNOLOGY OF MANUFACTURING AND ADVANCEMENT OF TECHNOLOGY FOR TURBINE ENGINE COATINGS (MANUFACTURING AND ADVANCEMENT TECHNOLOGY FOR TURBINE ENGINE COATINGS)
Williamson, J. R.
Air Force Systems Command, Wright-Patterson AFB, Ohio (AJ773273)
000970 Init- in AGARD Advanced Technology for Production of Aerospace Eng. Sep. 1970 /See N71-11626 [illegible] Refs Avail- NTIS

63 AD-697 686
HEAT-RESISTANT INORGANIC COATINGS (SELECTED PORTIONS)
Appen, A. A.
Foreign Technology Div Wright-Patterson AFB Ohio (141600) Rept No: FTD-MT-24-497-68, 22 Jul 69, 196p, Project: FTD-[illegible], Edited machine trans. of mono. Temperaturoustoichivye Neorganicheskie Pokrytiya, Leningrad, 1967 pi-106, 194-207, 215-239,

64 PB-262 616-T/SL
WORKS OF SEMINAR ON HIGH TEMPERATURE PROTECTIVE COATINGS (3rd) HELD AT LENINGRAD, ON 27-31 MAY 1966
National Bureau of Standards, Washington, DC.*National Science Foundation, Washington, DC. Special Foreign Currency Science Information Program (240 800)
Rept No: TT-74-53388, 1968, 677p, Monitor: 18, Trans. of mono. Temperaturoustoichive Zashchite Pokrytiya. Trudy III Seminara po Zharostoikim Pokrytiyam. Leningrad 27-31 May 1966, 1968 353p. Sponsored in part by National Science Foundation, Washington, DC. Special Foreign Currency Science Information Program.

65 N67-31162 NASA Issue 17 Category 17
DEVELOPMENT OF PROTECTIVE COATINGS FOR CHROMIUM-BASE ALLOYS SEMIANNUAL PROGRESS REPORT (FEASIBILITY OF USING DUCTILE NICKEL-CHROMIUM ALLOY CLADDINGS TO PROTECT CHROMIUM ALLOY TURBINE VANES AND BLADES)
Bartlett, E. S.; English, J. J.; MacMillan, C. A.; Williams, D. N.
Battelle Memorial Inst. Columbus, Ohio. (BE112895)
NASA-CR-85869; SAP-2 200766 NAS3-7612 20 JUL. 1966 47 p CFSTI

C: FRICTION AND WEAR

66 N79-17916/4SL
METHOD OF MAKING BEARING MATERIALS
Sliney, H. E.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Patent, Rept no: PATENT-4 136 211, PAT-APPL-860 406, Filed 13 Dec 77, patented 23 Jan 79, 5p, Monitor: 18, Supersedes PAT-APPL-860 406-77, This Government-owned invention available for U.S. licensing and, possibly, for foreign licensing. Copy of patent available Commissioner of Patents, Washington, DC. 20231

67 N79-15184/1SL
Effect of Nitrogen-Containing Plasma on Adherence, Friction, and Wear of Radiofrequency-Sputtered Titanium Carbide Coatings
Brainard, W. A.; Wheeler, D. R.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TP-1377, E-9681, Jan 79, 21p, Monitor: 18.

68 N79-20220/6SL
ADHERENCE OF SPUTTERED TITANIUM CARBIDES
Brainard, W. A.; Wheeler, D. R.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-79117, E-9950, 1979, 10p, Monitor: 18, Conf-Presented at the Intern. Conf. on Met. Coatings, San Diego, Calif., 23-27 Apr. 1979,

69 N79-21387 NASA Issue 12 Category 37
WEAR-RESISTANT BALL BEARINGS FOR SPACE APPLICATIONS - COATED WITH TITANIUM CARBIDE
Boving, H.; Hintermann, H. E.; Haenni, W.; Bondivenne, E.; Boeto, M.; Conde, M.
Laboratoire Suisse de Recherches Horlogeres, Neuchatel (Switzerland). (LC724316) 770428 In NASA. Goddard Space Flight Center the 11th Aerospace Mech. Symp. p127-137 (See N79-21374 12-37) AD(ESA, Frascati, Italy) AE(CNES, Toulouse, France) AF(CNES, Toulouse, France) 11p. Jpn. 1567 HC A11/MF A01

70 N79-23244 NASA Issue 14 Category 27
METAL BONDED CARBIDES FOR WEAR RESISTANT SURFACES
Norris, L. F.; Silins, V.; Adamovic, M.; Clegg, M. A.
Sherritt Gordon Mines Ltd., Fort Saskatchewan (Alberta). (SJ330184) 790300 In AGARD Advan. Fabric. Processes 12p (See N79-23236 14-31) 12p. Jpn. 1829 HC A12/MF A01

71 N79-20240/4SL
WIDE-TEMPERATURE-SPECTRUM SELF-LUBRICATING COATINGS PREPARED BY PLASMA SPRAYING
Sliney, H. E.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-79113, E-9945, 1979, 10p, Monitor: 18, Conf-Presented at the Intern. Conf. on Met. Coatings, San Diego, Calif., 23-27 Apr. 1979; Cosponsored by the AM. Vacuum Soc. and the AM. Soc. for Metals,

72 N78-26177/3SL
THE FRICTION AND WEAR PROPERTIES OF SPUTTERED HARD REFRACTORY COMPOUNDS
Brainard, W. A.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-78895, E-9368, Aug 78, 17p, Monitor: 18, Conf. Proposed for Presentation at the 2D Intern. Conf. on Solid Lubrication, Denver, 14-18 Aug. 1978; Sponsored by the AM. Soc. of Lub. Engr,

73 AD-A061 775/3SL
MATERIALS RESEARCH FOR ADVANCED INERTIAL INSTRUMENTATION. TASK 2. GAS BEARING MATERIAL DEVELOPMENT BY SURFACE MODIFICATION OF BERYLLIUM
Palmieri, J. R.
Charles Stark Draper Lab Inc Cambridge MA (408386)
Technical Rept. No. 1, 30 Sep 77-30 Jun 78, Rept No: R-1199, Sep 78, 38p, Contract: N00014-77-C-0388, Monitor: 18, See also Task 3, AD-A058 690.

74 N78-20338/7SL
FRICTION AND WEAR OF RADIOFREQUENCY-SPUTTERED BORIDES, SILICIDES, AND CARBIDES
Brainard, W. A.; Wheeler, D. R.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TP-1156, E-9384, Apr 78, 19p, Monitor: 18,

75 N79-22524 NASA Issue 13 Category 37
PERFORMANCE OF LUBRICANTS: OILS AND GREASES ON WEAR TESTS, COMPACT MATERIALS IN BALL BEARINGS, AND SPUTTERED COATINGS ON GAS-BEARING COUPONS
Final Report, 2 Jan. 1975 - 14 Apr. 1978
Mecklenburg, K. R.
Midwest Research Inst., Kansas City, Mo. (MZ513670)
AD-A063987; AFML-TR-78-126 780900 F33615-75-C-5116 93p. Jpn. 1725 HC A05/MF A01

76 N78-15229/5SL
FRICTION AND WEAR OF SEVERAL COMPRESSOR GAS-PATH SEAL MOVEMENTS
Bill, R. C.; Wisander, D. W.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TP-1128, E-9276, Jan 78, 42p, Monitor: 18, NTIS

77 N78-19038 NASA Issue 9 Category 37
WEAR-RESISTANT BALL BEARINGS FOR SPACE APPLICATIONS
Boving, H.; Hintermann, H. E.; Hanni, W.; Bondivenne, E.; Boeto, M.; Conde, E.
Laboratoire Suisse de Recherches Horogeres, Neuchatel (Switzerland) (LC724316)
770400 In NASA. Goddard Res. Center The 11th Aerospace Mech. Symp. p121-131 (See N-78-19026-09-99) AD(ESA) AE(CNES, Toulouse) AF(CNES, Toulouse) 11p. Jpn. 1245 HC A11/MF A01

78 N78-20333/8SL
COATINGS FOR WEAR AND LUBRICATION
Spalvins, T.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-78841, 1978, 32p, Monitor: 18, Conf-Presented at the 3D Intern. Conf. on Metallurgical Coatings, San Francisco 3-7 Apr. 1978; Sponsored by AM. Vacuum Soc. Inc.

79 N77-33348/2SL
X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF RADIOFREQUENCY-SPUTTERED TITANIUM CARBIDE, MOLYBDENUM CARBIDE, AND TITANIUM BORIDE COATINGS AND THEIR FRICTION PROPERTIES
Brainard, W. A.; Wheeler, D. R.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TP-1033, E-9102, Oct 77, 21p, Monitor: 18,

80 N78-20322/1SL
APPLIED RESEARCH PROGRAMME ON LUBRICATION OF TITANIUM BOLTS. REPORT ON IVD ALUMINIUM
Newnham, J.; Singh, K.; Curley, L.
Standard Pressed Steel Labs., Naas (Ireland)
Rept No: SPS-5229-4, ESA-CR(P)-1020, Oct 77, 31p, Contract: ESTEC-2670/76-NL-PP(SC). Monitor: 18,

81 N77-29226/6SL
X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF RADIOFREQUENCY SPUTTERED CHROMIUM BROMIDE, MOLYBDENUM DISILICIDE, AND MOLYBDENUM DISULFIDE COATINGS AND THEIR FRICTION PROPERTIES
Wheeler, D. R.; Brainard, W.A.
National Aeronautics and Space Administration, Cleveland, Ohio. Lewis Research Center
Rept No: NASA-TN-D-8482, E-9059, Aug 77, 21p, Monitor: 18.

82 AD-A048 191/1SL
NONDESTRUCTIBLE MESG PROGRAM
Taylor, K.
Charles Stark Draper Lab Inc Cambridge Mass (408386)
Final Rept. Jul 74-Jun 77, Rept No: R-1089, Aug 77, 69p, Contract: F33615-74-C-1234, Project: 666A, Task: 01, Monitor: AFAL-TR-77-159.

83 N78-19514/6SL
STUDY ON FRICTION AND WEAR PERFORMANCE OF ION-PLATED GOLD AND SILVER FILMS
Miaykawa, Y.; Nishimura, M.; Nosaka, M.; Miyawaki, Y.
National Aerospace Lab., Tokyo (Japan)
Rept No: NAL-TR-507, Jul 77, 105p, Monitor: 18, In Japanese; English Summary.

84 N77-24499/4SL
FRICTION AND WEAR PROPERTIES OF THREE HARD REFRACTORY COATINGS APPLIED BY RADIOFREQUENCY SPUTTERING
Brainard, W. A.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TN-D-8484, E-9055, May 77, 21p, Monitor: 18,

85 AD-A042 443/2SL
WEAR RESISTANT COATINGS FOR TITANIUM ALLOYS
Manty, B. A.; Liss, H. R.
Pratt and Whitney Aircraft Group West Palm Beach Fla Government Products Div (392887)
Final Rept. 15 Mar 76-15 Mar 77, Rept No: FR-8400, Mar 77, 74p, Contract: N00019-76-C-0342, Monitor: 18,

86 N77-19253/2SL
EFFECT OF ION-PLATED FILMS OF GERMANIUM AND SILICON ON FRICTION, WEAR, AND OXIDATION OF 52100 BEARING STEEL
Buckley, D. H.; Spalvins, T.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TN-D-8436, E-8953, Mar 77, 11p, Monitor: 18

87 AD-A036 444/8SL
WEAR CHARACTERISTICS OF SPUTTERED VERSUS ELECTROPLATED CHROMIUM ON ALUMINUM
Crowson, Andrew
Rock Island Arsenal Ill General Thomas J Rodman Lab (408247)
Technical rept, Rept No: RIA-R-TR-77-003, Jan 77, 27p, Monitor: 18

88 N77-18218/6SL
MICROSTRUCTURAL AND WEAR PROPERTIES OF SPUTTERED CARBIDES AND SILICIDES
Spalvins, T.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-X-73536, E-8842, 1977, 11p, Monitor: 18, Conf-to Be Presented at the Intern. Conf. on Wear of Materials, St. Louis, 25-27 Apr. 1977

89 PB-257 422/6SL
THE ROLE OF COATINGS IN THE PREVENTION OF MECHANICAL FAILURES. PROCEEDINGS OF THE MEETING OF THE MECHANICAL FAILURES PREVENTION GROUP (23rd) HELD AT THE NATIONAL BUREAU OF STANDARDS, GAITHERSBURG, MARYLAND, OCTOBER 29-31, 1975
Shives, T. R.; Willard, W. A.
National Bureau of Standards, Washington, DC. Metallurgy Div.* Office of Naval Research, Arlington, Va.*Naval Air Development Center, Warminster, Pa.*Frankford Arsenal,Philadelphia, Pa,*Federal Aviation Administration, Washington, D.C. (387 444)
Final Rept, Rept No: NBS-SP-452, Sep 76, 200p*, Monitor:18 Library of Congress Catalog Card No. 76-608258. Sponsored in part by Office of Naval Research, Arlington, Va., Naval Air Development Center, Warminster, Pa., Frankford Arsenal, Philadelphia, Pa., and Federal Aviation Administration, Washington, D. C.

90 AD-A041 861/6SL
THE TESTING OF PLASMA SPRAY COATINGS
Roseberry, T. J.; Onesto, E. J.; Dufrane, K. F.
Battelle Columbus Labs Ohio (407080)
Final Rept, May 76, 58p Contract: N00197-75-C-0060, Monitor: NOSL-MT-042

91 N76-22356/9SL
ADHESION AND FRICTION OF THIN METAL FILMS
Buckley, D. H.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TN-D-8230, E-8565, Apr 76, 19p, Monitor: 18

92 N78-23210 NASA Issue 14 Category 26
IMPROVING THE WEAR-RESISTANCE CHARACTERISTICS OF METAL SURFACES THROUGH VACUUM PRODUCTION TECHNIQUES
Bollinger, H.; Schulze, D.; Wilberg, R.
Addis Translations International, Portola Valey, Calif. (AB792197) BNWL-TR-277; CB-35431 770000
Transl. into ENGLISH from Neue Huette (East Ger.), V. 21, no. 3, Mar. 1976 p 145-149 Sponsored by DOE Prepared for Battelle Pacific Northwest Labs., Richard, Wash. 17 p. Jpn. 1823 HC A02/MF A01

93 BNWL-TR-277
IMPROVING THE WEAR-RESISTANCE CHARACTERISTICS OF METAL SURFACES THROUGH VACUUM PRODUCTION TECHNIQUES
Bollinger, H.; Schulze, D.; Wilberg, R.
Mar 76, 17p, Contract: EY-76-C-06-1830, Monitor: 18, Translated from Neue Huette 21 n3 p145-149 Mar 76

94 N76-14245/4SL
EFFECT OF NATURE OF OXYGEN INTERACTIONS ON FRICTION OF TITANIUM, ALUMINUM, AND MOLYBDENUM
Buckley, D. H.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TN-D-8123, E-8386, Jan 76, 17p, Monitor: 18,

95 IBK-14[illegible]
PLASMA SPRAY COATING HIGHER STRENGTH AND RESISTANCE TO WEAR, CORROSION AND EROSION
Spasic, Z.; Petrovic, M.; Polina, M.
Institut za Nuklearne Nauke Boris Kidric, Belgrade (Yugoslavia) ([illegible])
1976, 29p, Monitor: 18, Available in microfiche only. In Serbian, US. Sales Only

96 AD-A019 423/3SL
THE ADHESION, FRICTION, AND WEAR OF SPUTTERED TITANIUM CARBIDE COATINGS ON POLISHED STEEL SUBSTRATES
Ching-Yu-Wu, Lawrence
Illinois Univ at Urbana-Champaign Coordinated Science Lab*Electronic Systems Div., Hanscom AFB, Mass.*National Science Foundation, Washington, D.C. (09770
Technical Rept, Rept No: R-711, UILU-ENG-75-2247, Dec 75, 70p, Contract: DAAB07-72-C-0259, Grant: NSF-DMR74-15101, Monitor: 18

97 AD-A020 170/7SL
CERAMIC AIRFRAME BEARINGS
Vanwyk, Jan W.
Boeing Aerospace Co Seattle Wash (059610)
Final Rept. Jan 74-Nov 75, Rept No: D180-19181-1, 1 Nov 75, 87p, Contract: N00019-74-C-0[illegible], Monitor: 18,

98 N75-32463/2SL
PLASMA-SPRAYED, SELF-LUBRICATING COATINGS FOR USE FROM CRYOGENIC TEMPERATURES TO 870 DEG C (1600 Deg F)
Sliney, H. E.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-X-71798, E-8476, 1975, 13p, Monitor: 18

99 AD-753 985
AK-4 ANTIFRICTION PLASMA COATINGS
Truskov, P. F.; Kovalchuk, Yu. M.; Panamarchuk, V. G.; Onopko, V. S.
Foreign Technology Div Wright-Patterson AFB Ohio (141600)
Rept No: FTD-HT-23-1067-72, 17 Nov 72, 10p, Project: AF-7343, Monitor: 18, Edited trans. of Tekhnologiya i Organizatisiya Proizvodstva (USSR) n1 p71-72 1971, by Paul J. Reiff, Jr

100 N74-15122 NASA Issue 06 Category 15
INCREASING THE WEAR RESISTANCE OF COMPONENTS BY PLASMA SPUTTERING
Degtev, G. F.; Solovev, B. M.; Vashkevich, F. F.; Zhuravel, V. I.
British Library Lending Div., Boston Spa (England). (BZ232127)
BLL-RTS-7940 000273 Transl. into ENGLISH from Izv. Vyssh. Ucheb. Zaved., Mashinostro. (Moscow), v. 3, 1972 p 127-131 Jpn. 669 Avail: British Library Lending Div., Boston Spa, Engl.: LO.60 or 2 BLL photocopy coupons

101 AD-894 721/0SL
APPLICATION OF WEAR COATINGS TO GUN BARRELS
Bloom, John A.; Wakefield, Gene F.
Texas Instruments Inc Dallas (347 650)
Final technical rept. 16 Feb 70-15 Oct 71, Rept No: TI-04-71-11, Mar 72, 103p, Contract: F33615-70-C-1441, Project: AF-485-9, Monitor: AFML-TR-71-254, Distribution limitation now removed

102 N71-33248
A REVIEW OF SURFACE SEGREGATION, ADHESION AND FRICTION STUDIES PERFORMED ON COPPER-ALUMINUM, COPPER-TIN AND IRON-ALUMINUM ALLOYS
Buckley, D. H.; Ferrante, J.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-X-67900, E-6365, 1971, 18p, Conf- Proposed for Presentation at Lubrication Conf., Pittsburgh, Pa., 5-7 Oct. 1971, Sponsored by the Am. Soc. of Lubrication Engr. and the Am. Soc. of Mech. Engr, Auger Emission Spectroscopy, Low Energy Electron Diffraction, Sputtering Studies, and Adhesion and Friction Experiments on Single Crystals of Cu- SN, Cu- al, and Fe; al Alloys

103 N71-25508
LUBRICATION WITH SPUTTERED Mo S2 FILMS
Spalvins, T.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-X-67832, 1971, 15p, Conf- Proposed for Presentation at Intern. Conf. on Solid Lubrication, Denver, 24-27 1971, Sponsored by Am. Soc. of Lubrication Engr, Friction Experiments in Ultrahigh Vacuum to Evaluate Sputtered Mo S2 Film Lubricants.

104 AD-712 305
CERAMIC WEAR-RESISTANT COATING FOR ALUMINUM - PHASE I
Long, William D.
Army Materials and Mechanics Research Center Watertown Mass (403105)
Technical Rept, Rept No: AMMRC-TR-70-15, Jul 70, 19p*, Project: DA-1-T-062105-A-330,

105 N73-14605 NASA Issue 05 Category 18
THE ABRASIVE WEAR RESISTANCE OF VACUUM-CONDENSED COATINGS (ABRASIVE WEAR RESISTANCE OF VAPOR PLATED CHROME COATINGS)
Ilinskii, A. I.; Palatnik, L. S.; Sapelkin, N. P.
Air Force Systems Command, Wright-Patterson AFB, Ohio. (AJ773273)
AD-749769 FTD-MT-24-75-72 040872 AF PROJ. 7343 Foreign Technology Div. Transl. into ENGLISH from Zashch. Pokrytiya na Metal. (USSR) No. 3, 1970 p 201-204 Jpn. 567

106 N70-30156
FRICTION CHARACTERISTICS OF SPUTTERED SOLID FILM LUBRICANTS
Spalvins, T.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-X-52819, E-5706, 1970, 22p, Coefficient of Friction for Sputtered Solid Film Lubricants

107 N70-16819 NASA Issue 05 Category 15
RESEARCH AND DEVELOPMENT OF HIGH TEMPERATURE GAS BEARINGS. 2 - SELECTION AND EVALUATION OF GAS BEARING MATERIALS IN ARGON AT 900 F and 1400 F (HIGH TEMPERATURE TESTS TO DETERMINE SLIDING CONTACT EFFECT ON HYDRODYNAMIC CHARACTERISTICS OF TILTING PAD JOURNAL BEARINGS AND SPIRAL GROOVED THRUST GAS BEARINGS)
Murray, S. F.
Mechanical Technology, Inc., Latham, N.Y. (MQ990422)
NASA-CR-1477 001269 NAS3-9433 PLAC- Washington PUBL-NASA Date- Dec. 1969 Coll- 145p
Refs Avail- CFSTI

108 AD-845 190
AN EXPERIMENTAL PROCEDURE TO TEST SPUTTERED GOLD AS A SOLID FILM GEAR TOOTH LUBRICANT
Sampsel, Michael Martin
Naval Postgraduate School, Monterey, Calif (251 450)
Master's thesis, Sep 68, 52p, Distribution Limitation now Removed

109 N70-14363 NASA Issue 04 Category 17
WEAR RESISTANCE OF VAPOR-DEPOSITED COATINGS (WEAR RESISTANCE OF VAPOR-DEPOSITED CHROMIUM ALLOY COATINGS IN HIGH TEMPERATURE ENVIRONMENTS)
Sarkisyan, F.
Air Force Systems Command, Wright Patterson AFB, Ohio. (AJ773273)
AD-695890; FTD-MT-24-60-69 250469 Date 25 Apr. 1969 Coll 13p Refs Tran Transl. into English from Prom. Armenii/USSR/, No. 3-4, 1968 P 71-74 Avail CFSTI

110 N72-13489 NASA Issue 04 Category 18
SOME POSSIBILITIES FOR THE LESSENING OF WEAR BY STRATIFICATION (CARBIDE STRATA AND PLASMA-SPRAYED COATING PRODUCTION, AND FRICTION WEAR BEHAVIOR)
Steinhauser, S.
National Lending Library for Science and Technology, Boston Spa (England). (NJ552527)
NLL-T-6946-(5809.95) 170971 Transl. into English from East German report Presented at the ZIF Colloquy, East Germany, 1968 24 p Jpn. 498 Avail: Natl. Lending Library, Boston Spa, Engl.: 2 NLL photocopy coupons

111 N68-11644 NASA Issue 02 Category 17
DEPOSITION OF SPUTTERED MOLYBDENUM DISULFIDE FILMS AND FRICTION CHARACTERISTICS OF SUCH FILMS IN VACUUM (SPUTTERED MOLYBDENUM DISULFIDE FILM DEPOSITION AND FRICTION CHARACTERISTICS IN VACUUM)
Przybyszewski, J. S.; Spalvins, T.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio. (ND315753)
NASA-TN-D-4269 001267 129-03-13-02-22 PLAC- Washington Date- Dec. 1967 COLL- 14p Refs CFSTI

112 N65-16231 NASA Issue 06 Category 15
AN EVALUATION OF VAPOR-DEPOSITED TUNGSTEN TUBING TOPICAL REPORT (VAPOR-DEPOSITED TUNGSTEN TUBING IMPURITY CONTENT, RESISTANCE TO GRAIN GROWTH DURING HEAT TREATMENT, HARDNESS MEASUREMENTS, AND DUCTILE TO BRITTLE TRANSITION TEMPERATURE)
Lindgren, J. R.; Mills, R. G.; Weinberg, A. F.
General Dynamics Corp., San Diego, Calif. (GD201306)
NASA-CR-54277; GA-5721 191064 NAS3-4165 Cleveland, NASA. Lewis Res. Center, 19 Oct. 1964 39 p OTS

D: CORROSION AND EROSION

113 N79-23241 NASA Issue 14 Category 26
ION VAPOR DEPOSITED ALUMINUM COATINGS FOR IMPROVED CORROSION PROTECTION
Fannin, E. R.
McDonnell Aircraft Co., St. Louis, Mo. (MP532498)
790300 in AGARD Advan. Fabric. Proesses 8p (See N79-23236 14-31) 8p. Jpn. 1829 HC A12/MF A01

114 AD-A063 570/6SL
COATINGS FOR DIRECTIONALLY SOLIDIFIED GAMMA PRIME-GAMMA PLUS ALPHA EUTECTICS
Smeggil, John G.
United Technologies Research Center East Hartford CT (409252)
Final Rept. 1 Aug 77-31 Jul 78, Rept No: UTRC/R78-912959, 22 Oct 78, 50p, Contract: N00019-77-C-0424, Monitor: 18,

115 AD-A053 581/5SL
INVESTIGATING LOCALIZED CORROSION AND SPUTTERING FEASIBILITY OF AMORPHOUS CHROMIUM-CONTAINING ALLOYS
Diegle, R. B.; Lineman, D. M.; Boyd, W. K.
Battelle Columbus Labs Ohio (407080)
Interim Technical Rept. 1 May 77-30 Apr 78, Apr 78, 50p, Contract: N00014-77-C-0488, Monitor 18,

116 AD-A066 084/5SL
INVESTIGATING LOCALIZED CORROSION AND SPUTTERING FEASIBILITY OF AMORPHOUS CHROMIUM-CONTAINING ALLOYS
Battelle Columbus Labs Ohio (407080)
Semiannual Status Rept, 25 Oct 77, 15p, Contract: N00014-77-C-0488, Monitor: 18

117 AD-A047 472/6SL
THE RESPONSE OF COATED STEELS TO CAVITATION IN CORROSIVE ENVIRONMENTS
Herman, H.; Clayton, C.; Agarwal, S.; Safai, S.; Vargas, J.
State Univ of New York at Stony Brook Dept of Materials Sciences (401074)
Technical Rept, Rept No: TR-2, May 77, 62p, Contract: N00014-75-C-1018, Monitor: 18,
Availability: Microfiche copies only

118 AD-A033 096/9SL
GRAIN BOUNDARY SEGREGATION AND STRESS CORROSION CRACKING OF ALUMINUM ALLOYS
Green, J A. S.; Viswanadham, R. K.; Sun, T. S.; Montague, W. G.
Martin Technical Rept, Rept No: MML-TR-76-84C, Nov 76, 25p, Contract: N00014-74-C-0277, Monitor: 18

119 AD-A033 253/6SL
CORROSION FATIGUE BEHAVIOR OF COATED 5340 STEEL FOR BLADE RETENTION BOLTS OF THE AH-1G HELICOPTER
Levy, Milton; Morrossi, Joseph L.
Army Materials and Mechanics Research Center Watertown Mass (403105)
Final Rept, Rept No: AMMRC-TR-76-34, Oct 76, 16p, Monitor: 18

120 AD-A026 293/1SL
RESPONSE OF COATED STEELS TO CAVITATION IN CORROSIVE ENVIRONMENTS
Preece, C. M.; Herman, H.; Wilms, V.; Safai, S.; Fauty, J.
State Univ of New York at Stony Brook Dept of Materials Sciences (401074)
Technical Rept, Rept No: TR-1, May 76, 28p, Contract: N00014-75-C-1018, Project: NR-036-110, Monitor: 18

121 AD-A024 894/8SL
DEVELOPMENT OF EROSION RESISTANT CLADDINGS FOR HELICOPTER ROTOR BLADES
Moore, Victor S.; Stetson, Alvin R.
Solar San Diego Calif (326550)
Final Summary Rept. 2 Jan 74-30 Nov 75, Rept No: RDR-1788-2, Mar 76, 112p, Contract: DAAG46-74-C-0054, Project: DA-1748017, Monitor: DRSAV-76-16, AMMRC-CTR-76-9

122 AD-A022 344/6SL
EROSION AND FATIGUE BEHAVIOR OF COATED TITANIUM ALLOYS FOR GAS TURBINE ENGINE COMPRESSOR APPLICATIONS
Levy, Milton; Morrossi, Joseph L.
Army Materials and Mechanics Research Center Watertown Mass (403105)
Final Rept, Rept No: AMMRC-TR-76-4, Feb 76, 21p, Project: DA-1-T-162105-AH-84, Monitor 18,
See also Report dated Dec 70, AD-726 954

123 AD-A026 039/8SL
CHEMICALLY VAPOR DEPOSITED TUNGSTEN COATINGS FOR EROSION PROJECTION
Haskell, R. W.; Imam, A. R.
Watervliet Arsenal N Y Benet Weapons Lab (371075)
1976, 15p, Monitor: 18

124 AD-A015 037/5SL
POTENTIAL OF SPUTTERED FILMS AS PROTECTIVE COATINGS
Gentner, K.
Naval Air Development Center Warminster Pa Air Vehicle Technology Dept (407207)
Phase Rept, Rept No: NADC-75038-30, 21 May 75, 46p, Project: ZR022-06, Monitor: 18

125 N72-26813 NASA Issue 16 Category 18
POTENTIAL OF THIN, SPUTTERED FILMS AS EROSION RESISTANT PROTECTIVE COATINGS PT 1
Gentner, K.; Newhart, J. E.
Naval Air Development Center, Warminster, Pa. (N0000154)
000474 In NBS The Role of Cavitation in Mech. Failures p 117-128 (See N74-26800 16-12)
Prepared in cooperation with Naval Air Prouulsion Test Center, Trenton Jpn. 1095

126 N72-22545 NASA Issue 13 Category 17
STRESS CORROSION CRACKING BEHAVIOR OF TUNGSTEN FILAMENT REINFORCED U-4 1/2 Wt PERCENT Nb
(STRESS CORROSION CRACKING BEHAVIOR OF TUNGSTEN FILAMENT REINFORCED URANIUM ALLOY
CONTAINING 4.5 wt PERCENT NIOBIUM)
Magnani, N. J.; Romero, H.; Miglionico, C. J.
Sandia Labs., Albuquerque, N. Mex. (SB899064)
SC-DR-710799 001171 Sponsored by AEC 15p Jpn. 1761

127 AD-722 006
SUBSTRATE CORROSION OF PLASMA COATED SURFACES
Calabrese, Salvadore, J.; Pan, Coda H. T.
Mechanical Technology Inc Latham N Y (224550)
Technical Rept, Rept No: MTI-71TR7, Feb 71, 21p*, Contract: N00014-71-C-0074

128 AD-871 429
MANUFACTURING TECHNIQUES FOR APPLICATION OF EROSION RESISTANT COATINGS TO TURBINE ENGINE
COMPRESSOR COMPONENTS
Grean, Harry M.
General Electric Co., West Lynn, Mass. Aircraft Engine Group (403589)
Final Rept. 1 Apr 68-30 Dec 69, May 70, 110p, Contract: F33615-68-C-1487, Project: AF-476-8,
Monitor: AFML-TR-70-114, Distribution Limitation now Removed

129 N70-35754
COMPATIBILITY TESTING OF CANDIDATE PROTECTIVE BARRIER COATINGS AND PERFORMANCE TESTING OF
FILTER VENT MATERIALS FINAL REPORT
McGrew, J. W.; Seetoo, W. R.
Rept No: NASA-CR-72603, 16 Jun 69, 54p, Contract: NAS3-11839, Research Center Date -
16 June 1969 Coll- 54p, Flame Sprayed Ceramic Aluminum and Zinc Coatings for Corrosion
Prevention of Tantalum Containment Vessel in Nuclear Reactor

130 N68-24317 NASA Issue 13 Category 17
CORROSION PROTECTION VIA FLAME SPRAYING (FLAME SPRAYING COATING PROCESS FOR IMPROVED
CORROSION RESISTANCE OF STEELS, CERAMICS, AND COMPOSITE MATERIALS)
Esty, C. C.; Mc Makin, W. H.; Wheildon, W. M.
Norton Co., Worcester, Mass. (N6789113)
000067 Date 1967 Coll- 38p Refs Conf Presented at AFML 50th Anniv. Symp. on Corrosion of
Mil. and Aerospace Equipment, Denver, 23-25 May 1967

131 AD-738 805
CORROSION RESISTANCE OF FASTENER COATINGS
Brown, Stanley R.
Naval Air Development Center Warminster Pa Aero Materials Dept (402998)
Progress Rept, Rept No: NADC-MA-7150, 11 Jan 72, 39p, Project: A320-5203/202-8/2F00-541-201

E: MECHANICAL PROPERTIES

132 N79-13046/4SL
LOW-CYCLE FATIGUE OF THERMAL-BARRIER COATINGS AT 982 DEG C
Kaufman, A.; Liebert, C. H.; Nachtigall, A. J.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rep No: NASA-TP-1322, E-9688, Dec 78, 20p, Monitor: 18

133 AD-A048 497/2SL
HIGH DURABILITY MISSILE DOMES
Gentilman, R.; Maquire, E.; Pappis, J.
Raytheon Co Waltham Mass Research Div (298320)
Interim technical rept. 1 Apr 76-30 Sep 77, Rept no: S-2284, Dec 77, 46p, Contract: N00014-76-C-0635, Monitor: 18

134 AD-A040 510/0SL
FRACTURE TOUGHNESS OF CVD ZnS
Shockey, D. A.; Towcliffe, D. J.; Dao, K.C.
Stanford Research Inst Menlo Park Calif (332500)
Topical Rept. Mar 77, 11p, Contract: N00014-76-C-0657, Monitor: 18

135 N77-16345/9SL
STUDY OF PROPERTIES OF SILICIDE BASED COATINGS FOR In-738 LC
Vanamerongen, H.
Central Lab. TNO, Delft (Netherlands)
NL-2 Programme. Final Report, Rept No: TNO-CL-76-56, 14 Jun 76. 36p, Monitor: 18

136 N75-15054/0SL
BEARING ENDURANCE TESTS IN VACUUM FOR SPUTTERED MOLYBDENUM DISULFIDE FILMS
Spalvins, T.
National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio
Rept No: NASA-TM-X-3193, E-8166, Jan 75, 11p, Monitor: 18

137 N73-28598 NASA Issue 19 Category 18
MECHANICAL PROPERTIES OF THERMAL BARRIER MATERIALS PROGRAM-FINAL REPORT, 15 Jan. 1972 - 15 Feb. 1973/ (MICROSTRUCTURE AND MECHANICAL PROPERTIES OF THERMAL BARRIER MATERIALS PRODUCED BY ARC PLASMA SPRAYING)
Muszar, K. E.; Edenborough, N. B.
General Motors Corp., Indianapolis, Ind. Detroit Diesel Allison Div (GD073666)
AD-762045 DDAD-EDR-7786 000373 N00019-72-C-0148 Detroit Diesel Allison Div. 76p Jpn. 2312

138 N67-31223 NASA Issue 17 Category 17
EFFECTS OF ADDITIONS OF NONMETALLICS ON THE PROPERTIES OF VAPOR DEPOSITED TUNGSTEN (NONMETALLIC ADDITIVE EFFECTS ON PROPERTIES OF VAPOR DEPOSITED TUNGSTEN)
Chin, J.; Lindgren, J. R.; Weinberg, A. F.
General Dynamics Corp., San Diego, Calif. (GD201306)
NASA-CR-85906; GA-7324 001166 NAS3-6471 Nov. 1966 24p Refs Presented at the Houston Thermionic Conversion Specialist Conf., Houston, 2-4 Nov. 1966 CFSTI

F4 CUTTING TOOLS

139 AD-A024 342/8SL
SYNTHESIS OF NEW SUPERHARD MATERIALS AND THEIR APPLICATION TO CUTTING TOOLS
Bunshah, R. F.; Shabaik, A. H.
California Univ Los Angeles School of Engineering and Applied Science (404637)
Semi-Annual Rept. No. 3, 1 Apr-30 Sep 75, Rept No: UCLA-ENG-7612, 31 Oct 75, 41p,
Contract: F44620-74-C-0044, ARPA Order-2574, Monitor: AFOSR-TR-76-0321

140 AD-A015 873/3SL
SYNTHESIS OF NEW SUPERHARD MATERIALS AND THEIR APPLICATION TO CUTTING TOOLS
Bunshah, R. E.; Shabaik, A. H.
California Univ Los Angeles Dept of Materials*Air Force Office of Scientific Research,
Arlington, Va.*Advanced Research Projects Agency, Arlington, Va (406237)
Semi-Annual technical Rept. No. 2, 1 Sep 74-31 Mar 75, Rept No: UCLA-ENG-7559, Apr 75,
47p, Contract: F44620-74-C-0044, ARPA Order-2574, Monitor: AFOSR-TR-75-1382

141 N72-26408 NASA Issue 17 Category 15
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TUNGSTEN CARBIDE CUTTING TOOLS WITH TITANIUM CARBIDE)
Mah, G.; Wright, R. J.; Chapin, J. S.; Guller, J. E.
Dow Chemical Co., Golden, Colo. (D2799720)
RFP-1702 180272 at(29-1)-1106 Rocky Flats Div. 9p. Jpn. 2289

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EXPLORATORY DEVELOPMENT TO IMPROVE STANDARD CUTTING TOOL MATERIALS BY INFUSION WITH
METALLIC CARBIDES, CERAMIC OR DIAMOND
Schmidt, A. O.; Ham, Inyong
Pennsylvania State Univ., University Park. Dept. of Industrial Engineering (400 581)
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14. Abstract


This AGARD Lecture Series No.106 is sponsored by the Structures and Materials Panel of AGARD and is implemented by the Consultant and Exchange Programme.

In recent years, many new coating techniques have been coming into use, or are being developed, for applications where increased protection of engineering materials from the effects of corrosion, erosion and wear, particularly at high temperatures, is needed. This Lecture Series will be introduced with a review of the principles and the present state-of-the-art of applying metallic, ceramic and organic layers for these purposes, with particular emphasis on new techniques such as plasma spray, ion beam, laser etc. The resultant structure and properties of the coating layers and their interaction with the bulk material will be considered.

Lectures will also cover the behaviour of coated parts, as determined by the coating technique and material, and the effects in service of such aspects as corrosion, fatigue, tribology problems, structural stability etc. Finally, available techniques for the analysis and non-destructive evaluation of the composition, properties and soundness of the layers will be assessed.

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