Metallic and Ceramic Coatings

Production, High Temperature Properties and Applications

M G Hocking, V Vasantasree, and P S Sidky
Materials Department, Imperial College, London
Corrosion & Materials Consultants Ltd., London

Longman Scientific & Technical
Copublished in the United States with
John Wiley & Sons, Inc., New York

UTC 2002
General Electric v. United Technologies
IPR2016-01289

Longman Scientific & Technical
Longman Group UK Limited
Longman House, Burnt Mill, Harlow
Essex CM20 2JE, England
and Associated Companies throughout the world.

Copublished in the United States with
John Wiley & Sons Inc., 605 Third Avenue, New York, NY 10158

First published in 1989

British Library Cataloguing in Publication Data
Hocking, M.G.
Metallic and ceramic coatings: production, high
temperature properties and applications.
1. High temperature corrosion resistant coatings
I. Title II. Vasantasree, V. III. Sidky, P.S.
667'.9

ISBN 0-582-03305-5

Library of Congress Cataloguing in Publication Data available

Printed and Bound in Great Britain
at the Bath Press, Avon

Contents

10.5. Coating Production Methods: Future Work

Foreword

Coatings enable the attributes of two or more materials [the substrate and the coatings(s)] to be combined to form a composite having characteristics not readily or economically available in a monolithic material. Examples are tribological properties and high strength coupled with corrosion resistance. In the high temperature field economic and technical pressures to achieve extended lives and greater reliability plus a need to conserve certain relatively scarce (and hence expensive) or strategic alloying elements, have dictated increasing recource to coatings. The evolution of stronger, more creep resistant alloys to enhance thermal efficiency resulted in loss of oxidation and corrosion resistance. The need for surface stabilization led to the growing need for coatings and rapid developments in the field of surface engineering. Operation of materials at progressively higher temperatures close to the melting points of conventional alloys, where adequate cooling leads to loss of efficiency, has led to the development of ceramic thermal barrier coatings. Coatings may also be essential in high temperature materials strengthed by fibres, to achieve compatibility between the matrix and reinforcement.

As in most fields of technology, the field of high temperatures has also witnessed the practical and sometimes serendipitous application of materials in advance of theoretical understanding of service problems. Between 1950 and 1970, very active scientific contributions were made to the development and use of high temperature materials and understanding of their response to their operating environment. The eighties saw a shift in emphasis to conservation of strategic materials and studies of ways and means of minimising loss and damage to expensive components with attendant loss of operating time and revenue. Although the literature on coatings can be traced back to the era of electro-deposition in general, and aluminising of iron in the early forties, much of the information on coatings relevant to achievement of optimum high temperature performance – production, control and replacement economics – has accumulated significantly in the seventies and to date. This book surveys the means of production of coatings, and their application over the broad range of high temperatures, above 400°C. The coating techniques discussed however, are actually used on substrates employed over entire groups of temperature ranges, from cryogenic to very high temperature. Thus the methods presented are selectively adapted in practice, for use as and on semi-conductor materials both in the regular and the rapidly growing areas of VLSI-components and surface mounting technology, as well as on materials used in power and energy generation and tribology.

The authors are to be congratulated on their diligence and scholarship in bringing together such a comprehensive survey in the important field of surface engineering in high temperature technology.

J.F.G. Condé
Senior Consultant, lately
Head, Metallurgy & Ceramics Division
Admiralty Research Establishment,
PEMoD, Holton Heath, Poole, Dorset, UK.

Preface

Definite limits are being approached, or have been reached, in single materials development. A solution is to produce a composite material which combines the best properties of different metals or ceramics. This may be a coating of one material on another. Hybrid materials bring their own problems, especially in property matching at the interface, and coatings technology has thus emerged as a challenging field both for the fundamental and applied research worker.

This book was written to fill a long-existing need for a comprehensive source of information on metallic and ceramic coatings with all basic information and data presented in one compendium. Coating production methods as well as their application in various environments are discussed, with emphasis directed towards their high temperature properties. The first chapter gives the background, and the range of high temperature application of coatings is indicated in Chapter 2. Chapters 3–6 survey the several techniques available for the production of coatings of various kinds and thicknesses on both metallic and ceramic substrates. Coatings properties are surveyed in the next two chapters – physical properties in Chapter 7 and chemical behaviour in Chapter 8. The influence of mechanical and thermal factors are interwoven in both these chapters. Coating testing and inspection methods: NDT, microscopy and spectroscopy and coating repair are discussed in Chapter 9 along with a tabulation of coatings function in the various high temperature areas. Chapter 10 surveys the success record of high temperature coating application, its role in saving strategic metals together with the scope of coating technology and further areas for investigation.

A survey book of this nature aims to be a comprehensive source of an enormous amount of information. The need for brevity restricts descriptive discussions. A general bibliography is given which provides material for further reading on much of the basic information given here. A separate list is provided of more than 2000 references referred to in the text. These and related papers of the same authors were used in reviewing the specific topics concerned. Further references to the work of individual authors can be accessed through the references listed. The literature output in the fields of fuel-cell and semi-conductor technology has been prolific, and their pace of expansion needs to be justified with a survey exclusively devoted to them. References in this area have been kept peripheral and a number of diagrams and tables have been edited and redrawn to suit the requirements of this book. The authors would like to extend a collective acknowledgement to all those whose contribution and expertise have made this review possible. Tables, figures, specific information and or data adapted for this book are acknowleged with a reference to the authors by the usual norm of scientific publication. Thanks are also due to Elsevier Sequoia and to Dr. G. Perugini for granting permission for the reproduction of figures 2.4 to 2.7 and 8.30.

If this book proves useful to industrialists and practicing engineers who seek state-of-the-art information, provides the junior and senior academic population with good information on the sources and background in both theoretical and practical fields in metallic and ceramic coatings and surface modification, and offers ideas and relevant lines of investigation to investigators who look for areas of further work, then the authors' efforts have been worthwhile.

Our special thanks are due to Mr J.F.G. Condé for writing a foreword to the book, and to all our colleagues in the Departments of Materials and of Mechanical Engineering at Imperial College, for their help and co-operation at various stages of its preparation.

The Authors
February 1989

CHAPTER 1

High temperature coatings – the background

1.1. INTRODUCTION

A major challenge in technological development is to continue to meet requirements for new materials for use in progressively more stringent conditions. Usually one or more of a material's properties are incompatible with the conditions prevailing in the operating environment. In the material-environment configuration, the surface of a component is a vital parameter in determining its optimum usefulness. This is the basis for the development of coating technology.

The outermost surface and the rest of the component can be considered together to form a system. The primary requirement of a protective surface is to have qualities superior to that of the substrate in order to shield the component from an aggressive environment. The system is invariably hybrid, whether it has been achieved by means of a surface modification of the component substrate itself or one or more other materials have been applied as a coating to the component surface. In either case, surface treatment is involved, the choice of which is vast and varied. The combination of coated surface and substrate is called a coating system and it includes surface modification although it may be more accurate to designate the latter as a surface modified system.

The need for coating systems in the field of high temperature arose when improved performance criteria could not be met adequately in spite of new materials with superior physical, mechanical and metallurgical properties. Operating efficiency and production economy had to be considered and an improvement sought.

In this chapter a very brief account is given of high temperature materials and systems where coatings have been necessary for enhancing component endurance and thereby the system function.

1.2. HIGH TEMPERATURE MATERIALS

1.2.1. METALLIC MATERIALS:

High temperature metallic materials have developed rapidly beyond the early series of conventional ferrous alloys consisting of steels and stainless steels of various compositions, physical, thermal and mechanical history and microstructure. Chromium additions, up to 25 wt.% have been used and contribute to an improvement in high temperature strength and oxidation resistance of steels. Rupture strength increases were realised up to 340 MN m^{-2} with 15 wt.% Cr, and a higher temperature capability at 25 wt.%Cr at the cost of 100 MN m^{-2} drop in rupture strength. Ferrous alloy development is well documented and Fe-base alloys are satisfactory up to 1000°C under most oxidising conditions. Several high strength nickel- and cobalt-based alloys were developed in order to meet more complex high temperature corrosion phenomena. Superalloys - viz. Nimonics, Inco-alloy series, MAR- and Rene- series of cobalt alloys etc., came in the course of development of gas turbine alloys. Chromium content has been varied over a wide range from 10-50 wt.%, in the Fe-, Ni-, Co- based alloys but it is the effect on properties by all other additives viz. Al, Ti, Si, Mo, Nb, Hf, Y, Ce, Zr, W etc., that resulted in the considerable expansion of superalloy uses.

Superalloy components were prepared as cast and wrought, first by air melting and later by special vacuum melting procedures. Directional solidification, single crystal material preparation, the powder metallurgy route of fabrication (PM alloys), mechanical alloying (MAP alloys), dispersion strengthening and oxide dispersion strengthening (DS and ODS) have been the various other process routes resorted to in improving superalloy performance. High temperature creep, strength and corrosion resistance have been improved but the melting points of these alloys are still in the order of 1250-1300°C. Material improvements between 1940-1985 have yielded a 300 degrees (C) increase in turbine entry temperature, while the benefits of cooling have given an added advantage of operation up to about 1320°C (Byworth 1986; Alexander & Driver 1986). The role of alloying additives particularly those with m.p. above 1400°C in increasing the temperature range of superalloys has been examined (Jena & Chaturvedi 1984; Fleischer 1988). But a further increase in operating temperatures solely on the basis of superalloy component fabrication seems unlikely. Coatings are necessary.

Progress in the development of creep resistant refractory alloys, viz. Mo-, Nb-, Ta- and W-based alloys has been explored for space

-nuclear applications (Wadsworth et al 1988). Elements with high melting points such as C, Cr, Mo, Nb, V, W, Zr etc., fail due to excessive oxidation. Volatile oxide products and molten oxide formation are two other undesirable features (Table 1:1). Alloys of these can operate at high temperatures but when not threatened by oxidation. They are also brittle and component welding has been a problem. Coating failure on such alloys can be catastrophic. Metals with bcc structure have, in general, a ductile-brittle transition temperature (DBTT) giving poor mechanical properties at lower temperatures, resulting in cracking during thermal cycling. Additives modify DBTT, eg. Re added to Mo, W and Cr. Alternatives to Re and extensions of this beneficial effect are desirable, as are mechanistic studies of the phenomenon.

TABLE 1:1

HIGH TEMPERATURE MATERIAL CONSTITUENTS: MELTING POINTS

Element	Melting Point, °C	Element	Melting Point, °C
Al	660	Cr	1840
Mn	1260		
Si	1420	Nb	1950
Ni	1455	Rh	1960
Y	1475		
Co	1495	Hf	2200
		Ir	2440
Fe	1539	Mo	2620
Pd	1552	Ta	2850
Zr	1600		
V	1710	Re	3167
Ti	1725	W	3390
Pt	1769	C	3500

Cr,Pt,Si can form volatile oxides under certain conditions; C, W & Mo form gaseous oxides; Mo, Nb, Ta, W, & Zr undergo excessive oxidation; V forms molten oxides at >650°C; Ti dissolves oxygen. (Partington 1961)

Resistance heating elements function longer when coated, e.g. aluminized superalloy by surface oxidation self-protection. Other examples of oxidation protection are 18-8 stainless steels plasma sprayed with NiAl, siliconized refractory metals and plasma coated NiCr on steel used in annealing mills. High temperature metallic materials have to be assessed further but together with surface modification as a feature.

1.2.2. CERAMIC MATERIALS:

Ceramics appear at first an explorable alternative as high temperature materials because they have much higher melting points. Their brittleness is the principal drawback, and they are difficult to shape. Ceramics cannot function under conditions of mechanical and thermal shock (or cycling). Their high notch sensitivity renders them vulnerable to fracture under impact conditions. However, they have excellent corrosion resistance and low thermal conductivity. Ceramics are good candidates for thermal barrier materials. It is a two-fold problem to develop ceramics as coatings: to find the most suitable types of coating systems and to establish a satisfactory method of coating consolidation.

Ceramics are brittle (inductile) in that fracture occurs due to lack of significant plastic deformation (ductility) to absorb stresses by increasing the energy required for fracture propagation (Godfrey 1983/4). If a stress rate is high, e.g. explosive shock, it may exceed the dislocation propagation rate in a metal; the metal ductility then becomes irrelevant and it shows brittle behaviour; in this special case a ceramic may be stronger. But in general use, the non-ductile fracture behaviour of ceramics limits their use at high loads.

The low ductility of ceramics can be partly compensated for by a large modulus of elasticity, freedom of the microstructure from weak phases and a grain shape and size which maximises the work of fracture. Phase transformation toughening is also an area worth exploring. Big improvements in fracture toughness and microstructure free of holes and flaws has been achieved by hot pressing Si_3N_4 and SiC and adding a coating of a lower density reaction bonded surface layer containing Si (Kirchener & Seretsky 1974).

Large object impact on ceramics is destructive but in situations where only very small projectiles are possible, e.g. sand or dust erosion in an industrial compressor, hard ceramics perform much better than metals. Hot pressed silicon nitride eroded 5 times less than a superalloy in a dust erosion conditions test (Napier & Metcalfe 1977).

In general, above 1000°C ceramics have better strength, creep and oxidation resistance than superalloys. This temperature is considerably lower if comparison is made with ordinary alloys. Alumina has a high thermal expansion and thus undergoes thermal stress cracking; zirconia is stabilized by additives to reduce a destructive phase change at 1000°C, but thermal cycling above 1000°C may still cause problems. It also has a high thermal expansion but its low thermal conductivity and very high toughness and strength below 1000°C make it suitable for diesel engines, which operate in a maximum temperature zone of 800°C. A zirconia coating life depends on its tetragonal phase content, and methods of zirconia stabilization for diesel engine coatings have been discussed (Kvernes 1983).

SiC and silicon nitride have very low thermal expansion. At high temperature, oxidation evolves CO or N_2 which causes porosity in the protective layer on the ceramic. Above $1500^{o}C$ oxidation becomes severe. Production methods such as hot isostatic pressing (HIP), pyrolytic deposition and use of fugitive sinterers, e.g. Al in SiC, offer scope for further research. Sintering without pressing is feasible for Sialon, and materials comparable with hot pressed Si_3N_4 are obtainable (Godfrey 1983/4).

1.2.3. COMPOSITE MATERIALS:

The challenge for new materials has reached an exciting stage with the development of composites. Dispersion strengthened alloys, e.g. TD-NiCr, are the forerunners of the composite alloy group. Metal matrix composites (MMC) have advanced considerably from aerospace applications into light alloy technology, particularly the aluminium alloy series. Powder, particulates and fibres have been incorporated, mostly via the powder metallurgy route. Composites in matrices of Mg and Ti have also been tried but to a more limited extent. Ni- and Co- base alloys with incorporated oxides have been fabricated via the mechanical alloying route.

Although MMC materials have been available for the last two decades they are yet to be tested to their full potential for high temperature behaviour and as coating materials (Harris 1988; Stacey 1988). The development of carbon-carbon composites started in 1958 but intense research did not begin until the space shuttle project gathered momentum (Buckley 1988). Ceramic coatings for carbon composites was a logical consequent material modification in the process of optimising the application of the composite and combat its vulnerability to oxidation (Strife & Sheehan 1988). Composite coatings and composite/multilayer coatings have shown a considerable range and potential for development and application in the fields of high temperature and space technology (Wadsworth et al 1988; Das & Davis 1988; Lewis 1987).

1.2.4. RAPIDLY SOLIDIFIED MATERIALS:

Rapid solidification processing (RSP) of metallic materials has opened a totally new facet of alloy technology. The new materials were first called metallic glasses implying that their structure is amorphous. Materials prepared by RSP are mostly limited to narrow strips. The technique can be adapted to incorporate dispersed phases to consolidate the property advantages offered by MMC, and the conjoint product promises to provide a superior surface modification system yet to be fully explored (Hancock 1987; Metallurgia report,1987; Waterman 1987; Easterling, 1988). More details are given in section 1.6 of this chapter.

1.3. HIGH TEMPERATURE SYSTEMS.

1.3.1. GENERAL:

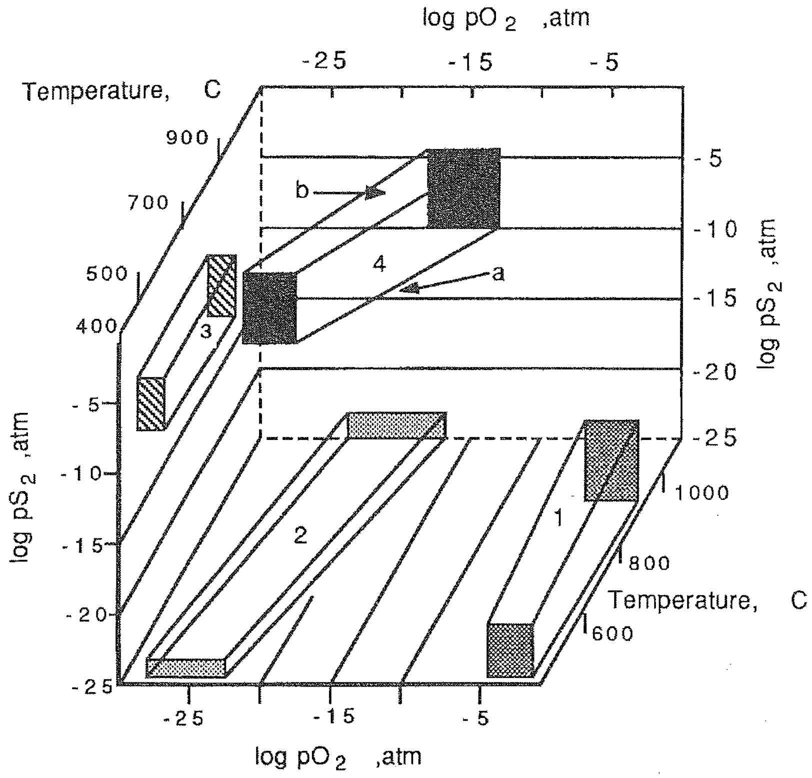
Power and energy systems where corrosion at high temperature is a severe problem are considered in this section. Component failure is often due to the synergistic action of several features in operation at high temperature conditions - the temperature and time scale of actual operation, local high temperature changes, the material used, the fuel employed, the prevailing environment and changes in it, mechanical and thermal stress cycles in the course of operation as well as shut down and rest periods. The insidious nature of high temperature corrosion lies in the fact that it causes a small section of the component to fail but the consequential costs for repair and re-installation stages are very high.

Lai (1985) gives a comprehensive survey of a number of other high temperature systems where molten salts, molten glass, hot metal and halogens comprise the corrosive media. Most of them use the high temperature alloys discussed here. A more detailed discussion on material degradation is given in a later chapter. Fig.1-1 indicates the prevailing conditions for a number of high temperature systems discussed below (Natesan, 1985).

1.3.2. COAL, OIL & FLUIDIZED-BED SYSTEMS:

Combined cycle electricity generation from coal gasification offers a potentially large increase in overall efficiency compared to the more conventional coal-fired and oil-fired boiler systems. Coal composition varies widely resulting in a wide range of chemical composition of both the gasifiable material as well as the ash and erodent products. Temperature regimes can extend from $350^{\circ}C$ for pressurised steam to fluid ash products at $1695^{\circ}C$ in combustion beds. Heat extractors operate at around $565^{\circ}C$ in general in the UK. A heat flux prevails; the evaporator tubes operate at a metal surface temperature of 450° while the superheater tubes go up to $650^{\circ}C$. Corrosion rates of 100-500 nm/h and in extreme cases >1000 nm/h have been recorded (Meadowcroft, 1987). The corrosive medium is aggressive to both Fe and Ni but not Cr.

The gasification process operates at much higher temperatures than boiler units. The physical conditions can thus be severe, with hot, abrasive-erosive particles and ash impingement. The chemical environment is predominantly reducing with oxygen potentials (pO_2) as low as 10^{-14} to 10^{-18} at a bed temperature of 850-$870^{\circ}C$. Sulphur potentials of 10^{-5} to 10^{-9}, and carbon activity of $3x10^{-3}$ (sometimes approaching unit activity), have also been recorded (Weber,1986). Coal gasification atmospheres may contain CO and H_2O, each 10%, H_2S 0.5% and balance N_2. 90% of the



1: Atmospheric fluidized-bed combustors & Pressurized fluidized-bed combustors turbines;
2: Gas-cooled Reactor; 3: Oil refining processes; 4: Coal gasification

Fig. 1-1: Prevalent Sulphur & Oxygen Partial Pressures over 400 - 1100 C in Various High Temperature systems

(Natesan 1985)

chloride content in coal emerges as 80 vol. ppm HCl during combustion (Meadowcroft,1987).

Attack by alkali sulphate phases stabilised with high localized potentials of SO_3 have been noted in coal-fired boilers. A large amount of Na_2SO_4 is the predominant corrodent in the combustion zone of black liquor boilers. Sulphur, alkali metals and vanadium cause catastrophic attack in oil-fired boilers. Sulphidation and oxidation by the action of H_2S and CO is the most common mode of attack. Chlorides promote low melting eutectics with sulphates, which affect low pressure boilers (100 bar) operating at 370°C. Laboratory simulations have not been informative enough to coordinate the chlorine effect in a predominantly reducing medium with H_2S at higher operating pressures and temperatures.

Several drawbacks appear in the use of materials in boiler and gasification fields. In brief, austenitic steels cannot be used on the chloride-containing water side because they are prone to stress corrosion cracking (SCC). Ferritic steels with 12% or less Cr are not cost-justified since they exhibit only a marginal improvement in corrosion resistance over mild steel. A higher chromium content in this alloy class results in embrittlement at 475°C. Heat exchangers of plain carbon steel, low alloy ferritic steels, e.g. Fe-2.25Cr-1Mo, and type 304 steel (18Cr-10Ni) suffer corrosive attack. Erosion-hot corrosion is also a major problem.

Improvements in performance require surface modification. Cladding has been used as a control measure. Ni-50Cr is used for structural members, and also for co-extrusion in black liquor boilers. Controlling excess air over that required for stoichiometric combustion, and fuel additives based on MgO control the medium to reduce vanadic corrosion. High-Cr alloys have shown good resistance to vanadic attack. Co-extruded tubes made from Incoloy 800H with an outer layer of Ni-50Cr has been effective. AISI type 310 steel (Fe-25Cr-20Ni) co-extruded over carbon steel or mild steel has been used mostly in boilers operating at lower pressures of 100 bar (Meadowcroft,1987; Stringer,1987). Fe-Cr-Al- alloys with and without pre-oxidation, MAP alloys and coatings have been tested to improve component performance (Weber,1986; Hocking & Sidky,1987).

1.3.3. GAS TURBINE & DIESEL ENGINE SYSTEMS:

Three main types of gas turbine may be listed: (i) Aero-engine, (ii) Industrial and (iii) Marine. Aero-engines burn clean fuel, but ingest impurities in the air-intake. This is aggravated in the marine-gas turbines since the air intake includes sea salt. Industrial engines burn inferior fuel containing vanadium and sodium, but the air intake can be filtered. Turbine components are made of Ni- or Co- based alloys. The blades and vanes are subject to cyclic temperature corrosion in alkali sulphate-oxide +/- chloride , +/- vanadic environment. Advanced turbines operate at high inlet temperatures (1350°C) and the industrial turbines at 1150°C. The blades are cooled to 850-900°C. Catastrophic corrosion occurs at lower temperatures 610-750° for Ni-based alloys and 750-850°C for Co-based alloys. Coatings have been tested extensively in the field of gas turbines and these include multi-component alloy compositions and alloy-ceramic formulae as well as thermal barrier coatings. Superalloys form 50 wt% of gas turbine engines, the rest being about equal parts of Ti-alloys, steels and composites. Development trends in the superalloy systems are inclined towards directional solidification (DS), powder metallurgy (PM) and mechanical alloy processing (MAP).

Diesel engines are the most fuel-efficient production heat engines. Exhaust valves, turbochargers and exhaust systems are subject to high temperature corrosion. Increasing efficiency by reducing heat losses has led to the concept of adiabatic diesel engines. Reducing heat losses from the cooling system, and in the combustion chamber, and harnessing the exhaust gas energy into work all demand thermal barrier surface modified systems which can offer durable and cost effective adiabatic diesel energy. Increase in operating efficiency has been attained by using gas turbine alloys, and design advances in airfoils and turbo-chargers (multi-stage and sequential). The corrosion problems are similar to those of industrial gas turbines (Fairbanks, 1987).

1.3.4. NUCLEAR POWER SYSTEMS:

Low-alloy carbon steels, ferritic and austenitic steels are some of the materials used in nuclear reactors, the selection for component fabrication depending on the temperature, environment and service conditions. Nuclear industry requires a fail-safe feature and cannot afford a major failure with catastrophic consequences. A high degree of predictability and reliability of component performance is vital and the temperature range is wide, from 100 to $650^{o}C$.

Fast breeder reactor systems in the UK use liquid sodium coolant. Despite control of coolant purity and cold-trap devices, circuits contain typically a few ppm oxygen which initiates product formation on the various austenitic AISI 316 stainless steel, low alloy steels, Stellite hardfacings (Co-based alloys) and IN-series (Ni-based) superalloys. Advanced gas-cooled reactor systems (AGR) use CO_2 as coolant and oxidation reactions predominate. Both the systems are subject to a number of tribological problems and rely on metallurgical coatings for long-term, maintenance-free service (Lewis,1987).

CHAPTER 2

High temperature coating systems

2.1. GENERAL

The predominant aspect of coating technology is the life expectancy of a coated system. System optimisation considers the coating composition, structure, porosity and adhesion together with operating and coating temperatures, substrate/coating compatibility, material availability and costs, coating renewal and in-service repair and maintenance aspects. Tables 2:1 and 2:2 give the requirements of a coating system for an optimum service life.

Weak coatings undergoing thickness loss may affect the mechanical properties of the substrate by effectively reducing the component total cross section. Interdiffusion may add or deplete alloy constituents. Thermal processing conditions may cause substrate microstructural changes and introduce residual stress. The system properties affected would be strength (in its various aspects), ductility, toughness, fatigue and creep resistance. Rapid temperature cycling has the greatest effect on the mechanical properties; temperature, exposure time and the environment interaction govern the chemical effects.

Mechanically bonded coatings often do not provide the required adherence. Diffusion bonded coatings are superior. A good example of a successful diffusion coating is the aluminide series applied to ferrous and many non-ferrous substrates alike.

TABLE 2:1

DESIRABLE PROPERTIES OF COATINGS & SELECTION CRITERIA

GAS TURBINE COATINGS	AEROSPACE COATINGS	NUCLEAR REACTORS
1. Adherent, Crack- and Pore-free.	1-8. All aspects indicated for gas turbines are valid.	1-8. All aspects indicated for gas turbines are valid.
2. Structure - Non-columnar & Defect tolerant.		
3. Microstructurally stable, Precipitation strengthened, no Brittle Intermetallics.		
4. Thermal expansion compatible to substrate, Resistance to Thermal Fatigue		
5. Predictable reaction & inter-diffusion with substrate which can be stopped or manipulated to suit requirements.		
6. Coating should not affect mechanical and structural properties of the substrate. Should improve bowing & cracking defects.		
7. Fatigue & Creep resistant		
8. Resistant to brittle fracture, DBTT at a low temperature.		
9. Isothermal & Cyclic - Oxidation (aircraft) & Hot Corrosion (marine & industrial) resistant; Impact & Erosion resistant; Intergranular corrosion resistant. Self-healing scratches and damages.	9. Hot Corrosion not such a threat. All other aspects indicated are applicable here.	9. Carburization and Hydrogen damage resistant. All other aspects indicated are valid Hot corrosion not considered Wear resistant and hardness coatings required.
10. Spall-resistant oxide scales; No molten reaction products; No vaporisation; have thermal barrier effect.	10. As in previous column.	10. Low neutron capture
11. Locally repairable, applicable to partly corroded items & cost effective.	11. In-situ repair difficult to implement. Otherwise repair and cost-effectiveness must be considered.	11. Increase fuel life & prevent burn up
		12. Drag-sliding protection in Magnox reactors.

TABLE 2:2

GENERAL PROPERTY CRITERIA FOR COATING SYSTEMS FOR HIGH TEMPERATURE SERVICE

Component System: Criteria/Property	Coating: Criteria/Property
Aerodynamic Property	Smooth surface finish for the coating. Must conform to the appearance of a precision cast blade.
Mechanical Strength and Microstructural Stability	Coating has to be resistant to all types of stress - impact, fatigue, creep and thermal, the system will be exposed to.
System Adhesion, Bonding & Interface Stability	Coating/Substrate must be compatible without gross thermal or structural mismatch. Diffusion rates at interface must be at a minimum at operating temperatures, and also composition changes. Development of embrittling phases must be avoided.
Surface Resistance to Erosion & Oxidation/Hot Corrosion	Coating composition must have sufficient reserve of all reactant constituents to meet scale reformation without a marked deterioration in protecting ability.Coating must be ductile, must develop uniform, adherent and ductile scale at low rates.

2.2. METALLIC COATING SYSTEMS

2.2.1. DIFFUSION COATINGS:

Aluminiding, is one of the first high temperature metallic coating systems. Alumina scale-forming coatings have given the best protection in high velocity gas turbines. Uncoated alloys containing Al as a minor constituent get fast depleted of it as Al diffuses to the surface to maintain alumina formation due to recurring oxide spallation. Diffusion-coated alloys form a surface alloy layer eg. NiAl and CoAl, which develop the protective alumina layer, under more controlled kinetics, and reform on spalling without affecting the substrate alloy properties. A renewal is possible before excessive depletion occurs. Brittle intermetallics can be a danger in this system.

A diffusion barrier layer between the coating and the substrat becomes necessary to prevent interdiffusion of elements withi the coating system. Multicomponent diffusion coatings (Al, B Cr, Si, Ti, Zr) to protect machines from liquid Al and for bras corrosion have been used (Samsonov, 1973). More work is needed i this area.

On steel, Al coatings are good up to 500°C, above which brittl intermetallics are formed. Thermal stress-induced cracks the propagate into the substrate metal. Aluminide coatings protec steel from oxidation and corrosion in hydrocarbon and sulphur containing atmospheres. Aluminised steel is better than stainles steel where oxidation carburization occurs (Sivakumar & Ra 1982). Chromised steel (diffused in) is air oxidation resistan up to 700°C. Above 800°C Cr diffuses into the steel reducin oxidation resistance. At higher temperatures brittle intermetal lics form. Good chromised sheet can be bent 180° without damag and is suitable for most firebox and heat exchanger application up to 600°C. Addition of Al or Si to the chromising pack proces confers oxidation resistance up to 900°C on mild steel, althoug continuous use at 900°C causes brittle intermetallics and conse quent cracking on thermal cycling.

On superalloys alumina-forming diffusion-bonded coatings provid an Al-rich surface to gas turbine environment. The superallo aluminiding involves more than one phase formation in the Ni-A (and Co-Al) systems. Heat treatment is given to stabilise th NiAl phase. NiAl with some Cr and Ti improve the hot corrosio resistance. Oxide particles, e.g. Y_2O_3, reduce spalling; defect like pinholes, blisters and cracks may be avoided by a combination of minor additives.

Aluminide coatings lack ductility below 750°C and on therma cycling, undergo surface cracking resulting in spalling of th alumina scale. To overcome these two problems the coating composition was adjusted to embed the brittle beta-NiAl or beta-CoA in a ductile gamma solid solution matrix. Addition of yttriu improved oxide adherence. Improvements in mechanical propertie were achieved by HIP-densified, argon-atomised pre-alloyed powde ingots; tensile ductilities of over 20% were produced by th smaller precipitate and its better distribution (Lane & Geye 1966). Much work was done on adding minor amounts of Si, Fe an Ti to improve the scale, but little improvement resulted (Uban 1977). Pt electroplate followed by aluminiding gives improve oxidation resistance which offsets the higher cost (Wing & McGil 1981).

Co-base superalloys for higher temperature but less stressed ga turbine vanes, have no Al and this limits the aluminide coatin thickness which can be applied without spalling. Superalloy com positions avoiding sigma and other embrittling phases can b destabilized by coating inter-diffusion (Boone 1981). Structura strengtheners like sub-micron oxides in ODS-alloys and carbide in DS-eutectic alloys can also limit coating selection (Jacobso

& Bunshah 1981). Further work is needed in these areas, increasingly, as higher performance alloys will narrow down the choice of acceptable coatings. In a recent 5 year period over 30 production coatings became necessary to replace an original selection of only one to two compositions (Boone 1981).

2.2.2. OVERLAY COATINGS:

Diffusion-type coatings, used successfully on early gas turbines, were tied to the substrate composition, microstructure and design. Later some changes were introduced - (i) in superalloy composition, such as reduction in Cr and increase in other refractory metals, (ii) in microstructure, by castings with more segregation, and (iii) in design, by air cooling and with thin walls (which introduced higher thermal stresses). These changes required coatings which were much more independent of the substrate. Overlay coatings met this necessity.

Overlay coatings also overcome the process restrictions encountered in diffusion coatings, especially the variants, viz. Cr/Al, Ta+Cr or the Pt-aluminides all of which give better stability and oxide-hot corrosion resistance than Al alone. MCrAlY compositions (M=Ni,Co,Fe alone or in combination) are the principals in the series of overlay coatings developed by electron beam evaporated physical vapour deposition (EBPVD) technique for multiple load use (Hill & Boone,1982; Hill,1976; Goward,1970). Fig.2-1 to 2-3 show the many composition variations produced. 3 million aerofoils have been successfully processed by EBPVD.

MCrAlY overlay used in gas turbines are usually Ni and/or Co with high Cr, 5-15% Al and Y addition around less than 1% for stability during cyclic oxidation. They are multi-phase alloys with ductile matrix, e.g. gamma Co-Cr, containing a high fraction of brittle phase, e.g. beta CoAl. The Cr provides oxidation hot corrosion resistance but too much Cr affects substrate phase stability. The success of most overlay coatings is the presence (and perhaps location) of oxygen-active elements like Y and Hf which promote alumina layer adherence during thermal cycling, giving increased coating protectivity at lower Al levels. Y mostly appears along grain boundaries if a MCrAlY is cast but is homogeneous if plasma sprayed. Thus MCrAlY with 12% Al are more protective than the more brittle diffusion aluminides with 30% Al.

Overlay claddings deposited by hot isostatic processing (HIP), electron beam evaporation or sputtering methods, are diffusion bonded at the substrate/coating interface, but the intention here is not to convert the whole coating thickness to NiAl or CoAl. There is thus more freedom in coating composition, whose properties can be maximised to the type required. Compositions based on NiCr, CoCr, NiCrAl, CoCrAl, NiCrAlY, CoCrAlY, FeCrAlY and NiCrSi have been successful in gas turbine engines. They are generally

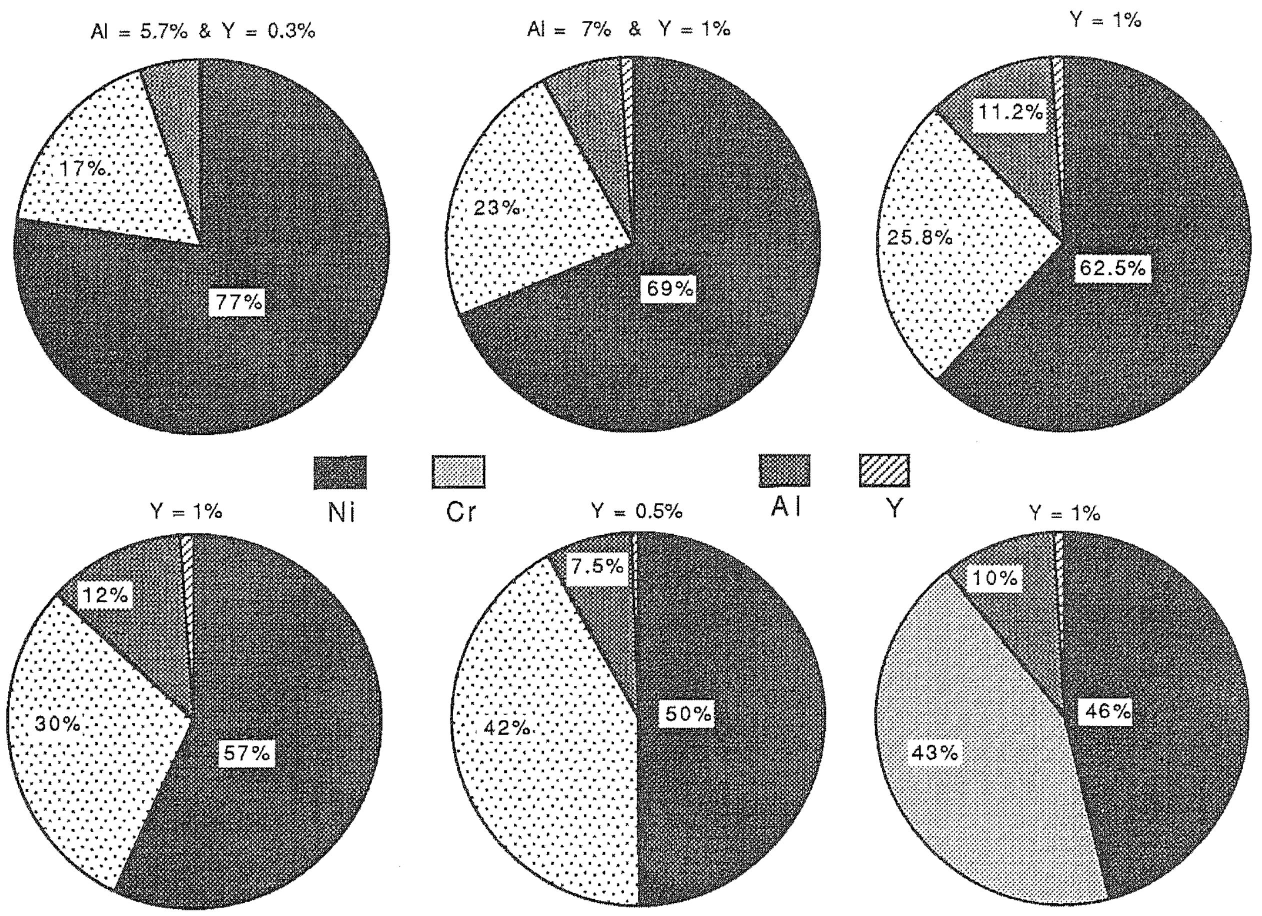


Fig.2-1: NiCrAlY COATING COMPOSITIONS , wt.% - A Selection of Coatings Tested on gas turbine blades

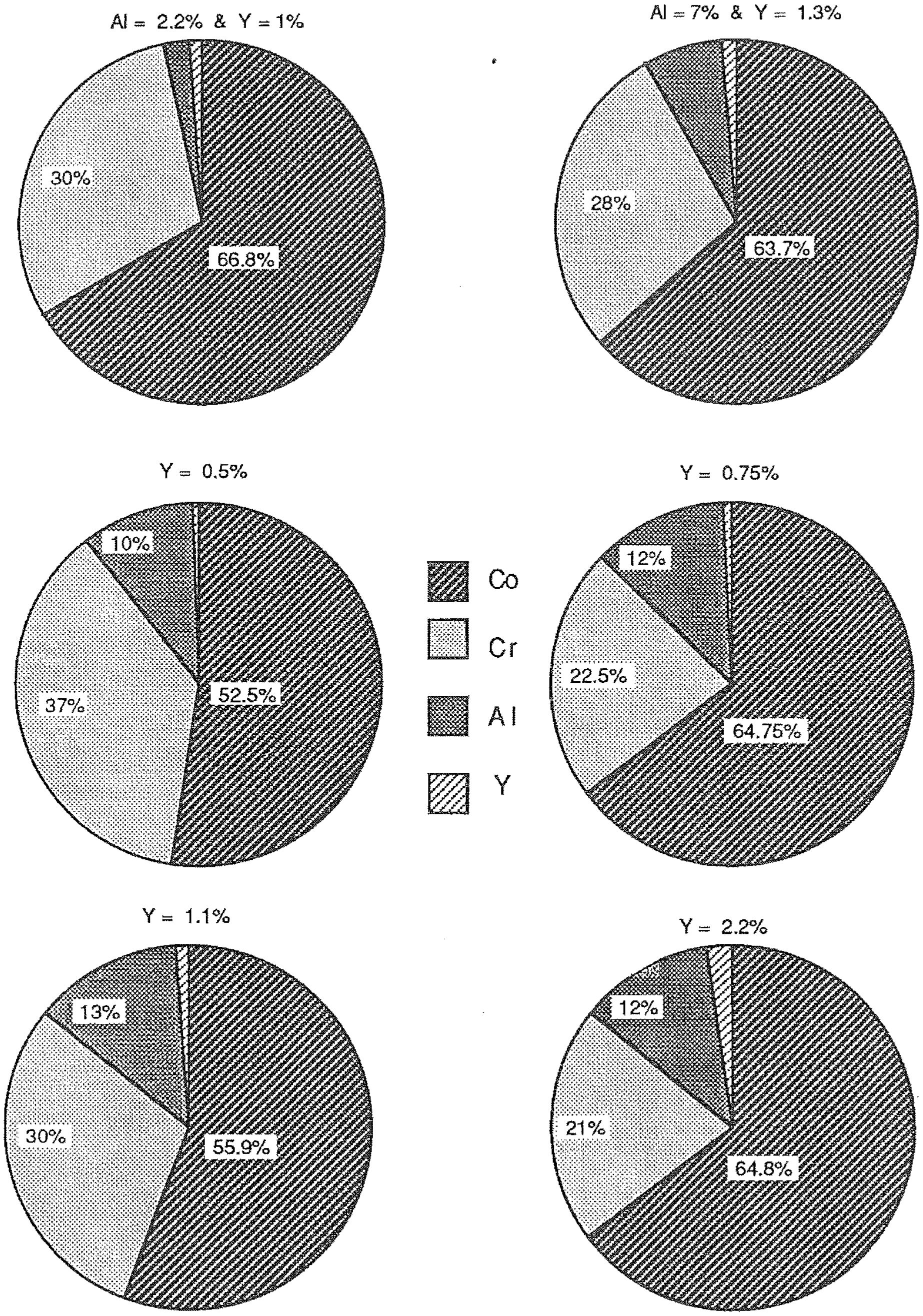


Fig.2-2: CoCrAlY Coating Compositions, wt.% - A Selection Tested on Gas Turbine Blades

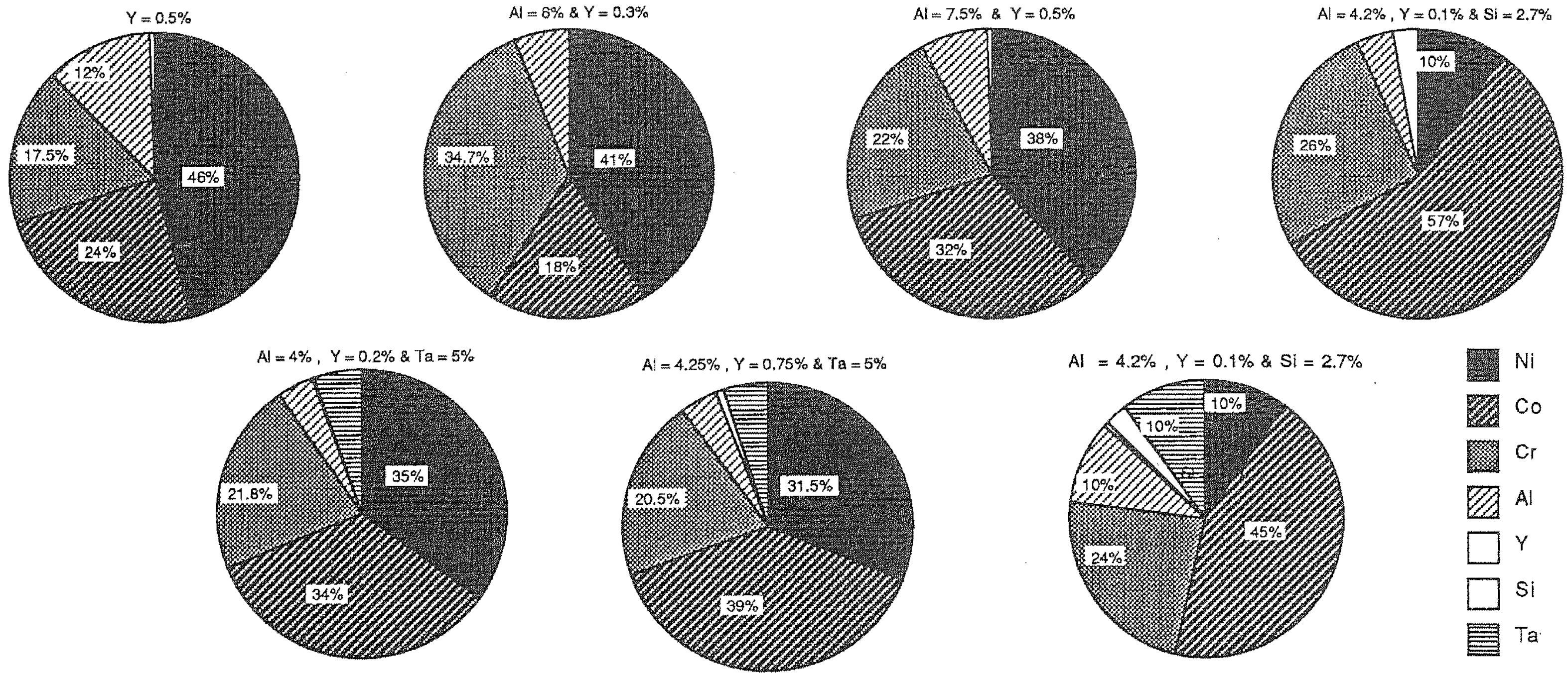


Fig.2-3: NiCoCrAlY Coating Compositions, wt.% - a Selection Tested on Gas Turbine Blades

alumina formers with only 10%Al unlike the 30% in nickel aluminide coatings. Cr increases the Al activity which allows this feature. Higher Al levels cause brittleness and a higher DBTT, and the Al levels are generally held below 12% (5-10% preferred). The coatings are also more ductile than NiAl and CoAl and can be rolled and bonded by HIP. In general, NiCrAlY give best results against high temperature oxidation while CoCrAlY are best for hot corrosion.

2.2.3. OTHER METALLIC COATINGS:

Refractory metals may be coated with oxidation resistant alloys such as Hf-Ta and Nb-Ti-Al-Cr which tend to deform without cracking and can withstand impact damage. If a Ta-containing coating is to be used on an alloy with a small carbon content, eg. IN 738, TaC will precipitate at the bondline and impair adhesion. This is prevented by using a Ni electroplate at the interface. Al foil placed at a superalloy/cladding interface acts as a source of Al for that lost into the oxide. It melts and diffusion bonding occurs simultaneously with formation of beta NiAl at the bondline (Lane & Gayer 1966). A refractory metal, e.g. Nb,Ta interlayer between NiAl and superalloy substrate prevents interdiffusion of Al and Ni (Lakhtin et al 1977).

Plasma sprayed coatings have a large fraction of open and closed porosity, which lowers strength and decreases resistance to corrosion. Heat treatment to reduce the porosity must avoid melting of a thin substrate or degradation of the substrate/coating interface. Even rapid CW-laser surface fusion may be unsatisfactory for air-sprayed coatings due to expansion of gas in the pores giving a sponge structure. Better results are obtained with a pulsed TEA laser which melts only the upper surface of the coating (Dallaire & Cielo 1982).

Ion implantation of Al in Fe reduces oxidation even when the oxide formed is much thicker than the ion implanted layer (Pons et al 1982). Y implantation in NiCr, FeNiCr and Fe41Ni25Cr10Al reduces oxidation and improves scale adherence, of interest for nuclear power materials (Pivin et al 1980). Ion implanted coatings produce results beyond what would be expected from just their shallow effective depth, e.g. Ce penetrates only 0.1 micron into stainless steel (Bennett 1981). Research is needed on the possible effects of ion bombardment damage, ion bombardment induced sputtering of the substrate (perhaps increasing the oxide nucleation sites giving smaller oxide grains with thus an increased and grain boundary diffusion).

Surface welded systems are used for wear and corrosion resistance. The thickness is usually at least 3 mm. Substrate preheating prevents weld distortion. Multilayer deposits of hard alloys can be interleaved with ductile layers to stop crack propagation. Laser surface melting modifies the surface structure and can improve strength, wear and corrosion resistance. Phase change or stabilization, structural changes, additive and amorphous alloy forming are several other features of coating systems achievable using laser as a "coating" tool (Gregory 1980).

2.2.4. METAL COATINGS ON CERAMICS:

Cu, Ni and Co can be cementation coated onto carbon fibres for aeronautical applications (Kulkarni et al 1979). A Cu layer beneath the Ni layer prevents Ni/C interaction (Shiota & Watanabe 1979) as C does not diffuse through Cu. Graphite can be protected by coatings of Ir (expensive metal). Metallising thermal barrier coatings for obtaining temperature monitoring contacts by surface thermocouples is another feature of ceramic substrate/metal coating systems. Joining a metal to ceramic or glass is achieved by high temperature means in the region of 1550°C (Jones 1985; Morrell & Nicholas 1984; Twentyman & Hancock 1981, Twentyman & Popper 1975; Twentyman 1975), and also at much lower temperatures, from 900 - 1100°C (Tomlinson 1986; Tentarelli et al 1966).

2.3. CERAMIC COATING SYSTEMS

2.3.1. GENERAL:

Ceramic coatings on metals is the major topic considered here. Some brief information is provided on ceramic-on-ceramic coating systems before concluding this section. Fig.2-4 and 2-5 show the extent of applications of ceramic coatings over a wide range of operating temperatures (Perugini 1976).

Ideal coatings which satisfy all the requirements of Table 2:2 do not exist and the use of good substrates is necessary to assist the coating. The choice of a coating, as in other coating systems, depends on the environment, substrate material, coating availability and cost. Ceramic coatings are used severally as thermal and corrosion barrier coatings as well as wear and erosion resistant and tribological coatings. Wear resistant coatings are very important even just on economic terms, e.g. in the U.S.A. the cost of machining is about $70 billion/year (1978), and the cost of tools is $900 million/year (about half divided between cemented carbide and high speed steel tools).

The scope of ceramic coatings in high temperature media has been discussed by Perugini (1976) and Eriksson et al (1982). Coatings for gas turbines have been reviewed (Godfrey et al 1983; Godfrey 1983/4,1981, 1978, & 1974). A survey of the requirements for diesel engines (Timoney 1978) and a review on coatings for diesel engines are available (Kvernes 1983).

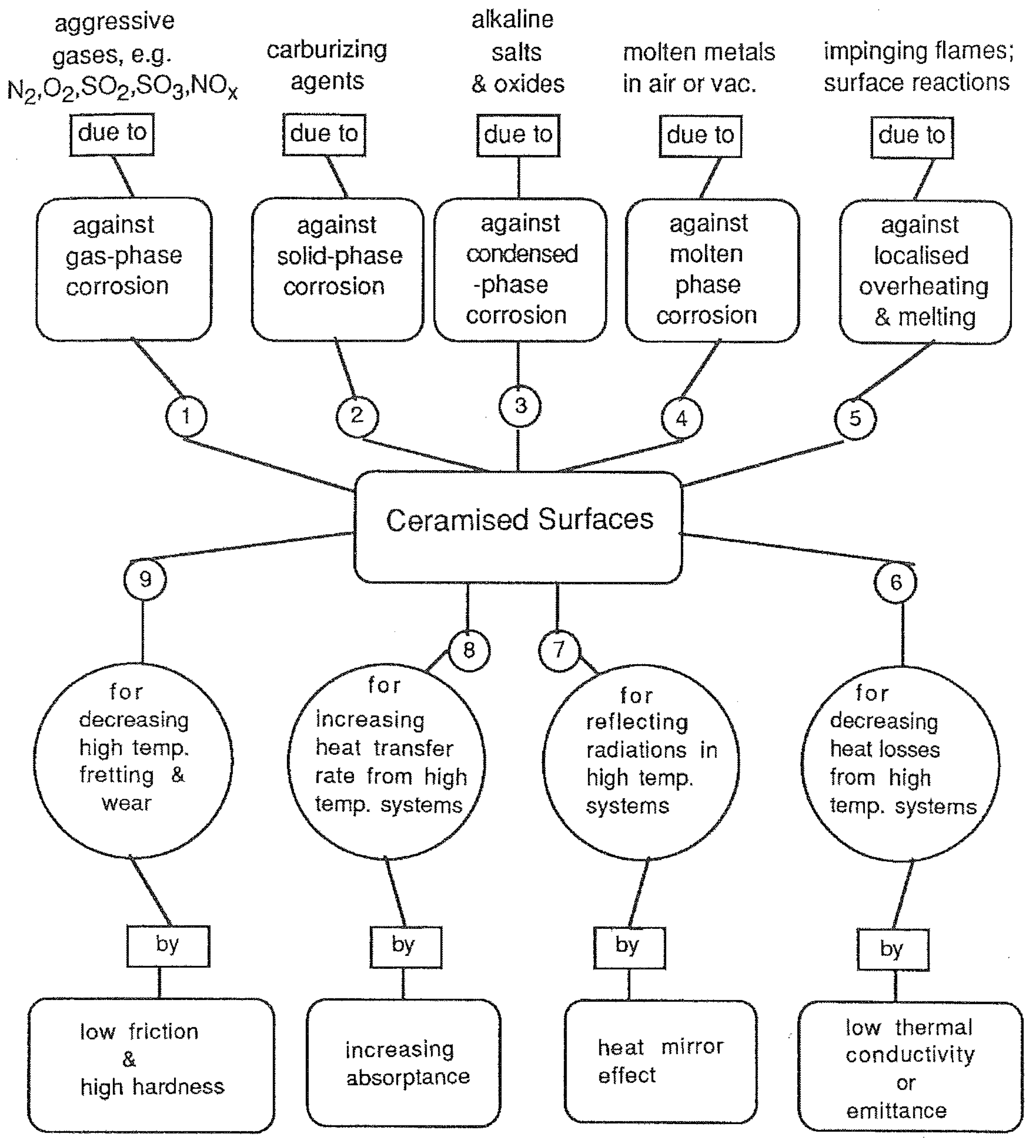
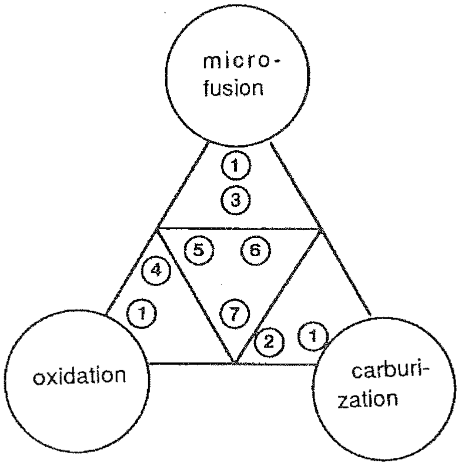
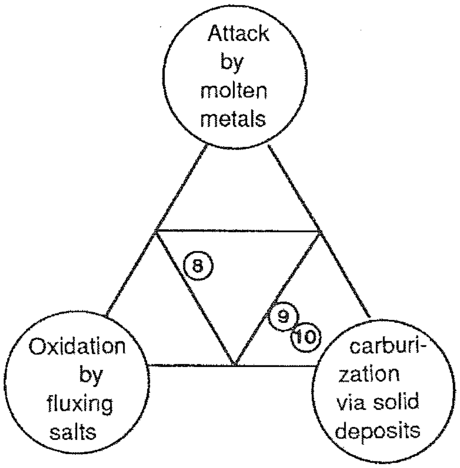


Fig.2-4: Ceramics & Their Role in High Temperature Environment

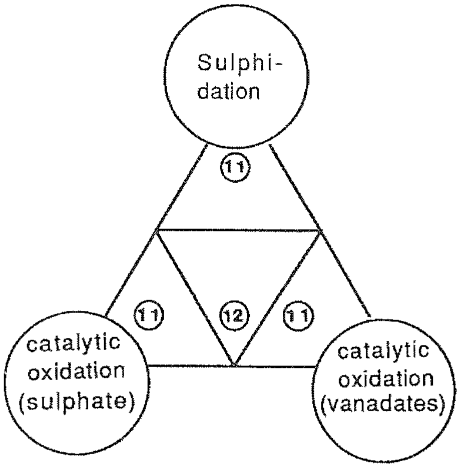
(Perugini 1976)



1. Burners & combustion chambers of reactors for the cracking of hydrocarbons in petrochemical industry.
2. Tube reactors of ethylene furnace in petrochemical industry.
3. Rocket nozzles.
4. Oxygen blow-pipe head in iron industry.
5. Piston heads; valves of big diesel engines.
6. Antipollution of thermal reactors in automobile industry.
7. Preheating or cooling manifolds.



8. Metallic parts under corrosive conditions. (caused by non-ferrous molten metals)
9. Metal moulds for casting iron and iron-alloys lubricated with graphite -additive oils.
10. Graphite crucibles for metallizing (eg. Al) under vacuum.



11. Industrial boiler tube configuration.
12. Sections operating under catastrophic corrosion conditions.

Fig.2-5: Applications of Ceramic Coatings in High Temperature Technology
(Perugini 1976)

Protection requirements for internal combustion engines include insulation of piston caps, shields for cylinder heads, top liner, exhaust ports and exhaust manifold. Improved high temperature lubrication and valve modifications are recommended, and development of ceramic cam followers offer advantages over metallic counterparts as the former are lighter than metals and thus may cause less wear. Plasma sprayed ZrO_2, liner inserts made of Al_2O_3 and ZrO_2, alumina titanate exhaust ports and ceramic bearings are being investigated. Si_3N_4 has excellent tribological properties (Godfrey & Taylor 1968; Burke et al 1978; Godfrey 1978; Hamburg et al 1981).

TiC has been coated on steel at 450^oC from Ti vapour and acetylene by activated reactive evaporation (ARE) (Raghuram & Bunshah 1982; Nimmagadda & Bunshah 1975) and at 300^oC by reactive sputtering (RS) (Nakamura et al 1974). TiN has been coated onto steel etc., using $Ti(NR_2)_4$, Ar, H_2, N_2 mixtures by chemical vapour deposition (CVD) (Sugiyama 1975) at $250-600^oC$, and using Ti vapour, N_2 (or NH_3) by ARE at 20^oC (Bunshah & Raghuram 1972). ZrO_2 has been coated onto Si using Zr acetylacetonate, O_2, He, at $450\ ^oC$ by CVD (Balog et al 1972; Sladek & Gilbert 1972). W_2C + W_3C have been deposited on steel from WF_6, C_6H_6, H_2 at $300-700^oC$ (Archer 1975). The wear of this tungsten carbide composite is second to only TiC. Ti(C,N) coatings have been deposited on stainless steel compressor blades at 600^oc by CVD from $TiCl_4$, $N(CH_3)_3$, N_2, H_2. Cr_7C_3 coatings are produced by CVD of dicumene chromium at 450^oC, with a thin interlayer of Ni to improve adhesion and mechanical properties of the system (Gates et al 1976). Other examples are summarised further in Chapter 4.

Future needs discussed by Mikoni & Green (1974) for oxidation resistance coatings for superalloys, refractory metals and graphite would be a useful source from which later developments may be checked. Many systems rely on Al_2O_3 or SiO_2 formation for protection, but multi-layer coatings offering resistance to corrosion and diffusion, coatings forming complex oxides, thermal barrier coatings and surface modifications to form dense glasses or incorporate dispersed oxides etc., have attracted much attention in recent years (Restall,1979; Nicholls & Hancock,1987; Stringer,1987; also see bibliography).

Ceramic coatings tend to be thick and brittle; they may also tend to devitrify. On thermal cycling the coatings tend to spall. But they offer excellent resistance to oxidation and corrosion and are suitable for static components like combustion liners, but further research is needed for use on rotating components. Ceramic coatings are often complex silicates with additions of ZrO_2, TiO_2, Al_2O_3, CeO_2, etc., and give protection up 1260^oC. Ni-CrSi are used on industrial turbines (Tamarin & Dodonova,1977) and a liquid Sn-Al phase has been used to seal all cracks and fissures in porous silicide coatings on Mo- and Nb- alloys (Stecher & Lux,1968; Priceman & Sama,1968). Nitrides have been widely investigated for wear resistance and thermal barrier layers. An improved approach indicated is to add elements to coatings to resist cracking and to extend tolerance to cracks if formed.

Steel coated with vitreous enamel is probably one of the earliest of ceramic-on-metal systems and has one of the best resistances to the high temperature corrosion of gas appliances. The surface is non-porous, hard and wear-resistant and useable up to 600°C. However, tensile cracks can occur due to inadequate thermal shock resistance or to impact. A design guide from the Vitreous Enamel Development Council (U.K.) recommends using low carbon steel, preferably zero carbon and enamelling steels, with good hot strength and enough thickness and radius to eliminate stress points. Ferrous alloy supports in kilns are coated with thermally sprayed Al_2O_3 or NiAl. Plasma coated NiCr on steel is used in annealing mills. Thermocouples need protection from oxidation, e.g. chromel-alumel, is coated with vitreous enamel.

Chlorine is bubbled through melts in Al production to purify it and the steel tube used reaches 650°C; ceramic coatings prevent corrosion of the tube by chlorine and Al. Casting channels and moulds for Al are iron-based materials coated with alumina or NiAl; W has been used with silica coatings, fused silica has been coated with alumina and alumina-coated iron has also been used for Al casting.

The most important properties for vacuum vessel materials are the adsorption and desorption rates of gases on the surface. These properties are strongly affected by the surface composition of materials. This was investigated using Auger electron spectroscopy for SUS321 stainless steel with TiC precipitated onto the surface and for laboratory melted SUS304 stainless steel doped with boron and nitrogen. The latter steel proved superior because it formed a hexagonal lamellar boron nitride precipitate on the surface which was inert to the surface and self-healing occured.

Plasma deposited coatings of dielectrics, especially refractory oxides, are good high temperature electrical insulators (Dudko et al 1982). The adhesion of plasma sprayed ceramics to metals is generally poor but can be considerably improved if a sprayed bond-coat or interlayer is used, e.g. NiAl, Mo (Campbell 1970). Refractory metals for aerospace and other applications are coated with silicides (MSi_2, M_5Si_3), aluminides, borides (HfB_2, ZrB_2, TiB_2) and oxides (ZrO_2, HfO_2, Al_2O_3 and ThO_2). AlB_{12} coatings on Mo and W wires are in use up to 1800K as thermoelectric converter components for nuclear reactors (Motojima et al 1981). Protection of Nb and Ta against carburization can be achieved by NbB_2 and TaB_2 coatings (Samsonov 1973).

Energy saving refractory coatings have high emissivity for furnace walls and roofs radiating heat back into the furnace. Consequent time and fuel saving reduce production costs. Pyrolytic carbon coatings on nuclear reactor fuel particles form a low permeability encapsulation for containing fission product gases (Anon., Metallurgia 1980,1981). SiC is not stable above 1500°C as a barrier to escape of fission products from nuclear fuel particles and ZrC-C mixtures have been proposed as an alternative (Ogawa et al 1979).

Extrusion dies plasma coated with Al_2O_3, ZrO_2, ZrB_2 and HfB_2 are used for W at 1800°C. But die life is short and improved coatings are needed. Ti is often glass coated for protection from contamination and from formation of the undesired alpha phase. But these coatings are hard to remove. Hot rolling requires thermally insulating coatings to avoid temperature drop of the billet and reduce furnace requirements for reheating between passes. Alumina and zirconia plasma sprayed coatings have been used for this purpose . Die casting of Al requires dies which last for over 10^5 injections and coatings are used of oxide layers generated either by oxidation during initial use or by wash coats. Steel die cores have been chromized to extend life about threefold mainly by improving the thermal resistance of the core materials. Coatings are needed for die casting steel; uncoated W or Mo alloy dies have been tried (Nat.Acd.Sci.Rep.1970).

2.3.2. OXIDATION RESISTANT CVD COATINGS:

Chromizing, aluminizing and siliconizing are widely used. The first two would be classed as metallics but silicides are more in the ceramic area. Siliconizing is good for refractory metals and alloys since $MoSi_2$, WSi_2 and VSi_2 have good oxidation resistance. Reactions between 20%Cr/25%Ni/Nb-stabilized stainless steel fuel cladding and the CO_2-based coolant in AGCR-s (Advanced Gas Cooled Reactor) causes oxidation of the steel and spalling of highly active oxide. C deposition from the CO_2 also affects heat transfer from the fuel pin. A coating can prevent these effects and factors include good heat transfer (thin coating, if ceramic), low neutron capture and no chemical interaction between coating and substrate. SiO_2 CVD coatings are used to protect 9% chrome steels from oxidation in high pressure CO_2 AGCR-s (Graham 1974; Brown et al 1978) but thermal shock cracks can occur.

CVD coatings of ZrC_xN_y are used for solar energy absorption, wear resistance for carbide cutting tools, and refractory protective coatings for nuclear fuel elements (Zirinsky & Irene 1978). Si_3N_4 CVD coatings are used on Mo (Galasso et al 1978). TiB_2 CVD coatings are very resistant to chemical and oxidation attack (Besmann & Spear 1977). Ti_5Si_3 CVD coating on Ti greatly reduces the oxidation rate but cracks occur after long times (Abba et al 1982).

A CVD SiO_2 coating on both clean and on corroded steel greatly reduced the oxidation rate (Brown et al 1978). A CVD SiO_2 coating on 20Cr25NiNb stainless steel reduced the oxidation rate by 5 times, in CO_2 at 825°C (Bennett et al 1982). Its good adherence prevented oxide spallation. This is important for use in AGC reactor fuel cladding, as spalled oxide would be radioactive. Ceria and Y or Ce ion implantation is an alternative.

Wear resistant CVD coatings are widely applied, e.g. diffusion coatings by case-hardening (Krier & Gunderson 1965): carburizing, nitriding, carbonitriding, siliconizing and chromizing. Boriding (Matuschka 1979) and ion-nitriding are also used. CVD of TiC, TiN and alumina occurs at over 800°C , too high for normal steels and Cu alloys. Research is needed to overcome this. The number of wear resistant CVD coatings below 800°C is very limited at present. W_2C and W_3C coatings are suitable for normal steel, being deposited (CVD) at 300-700°C (Archer & Yee 1976), and their wear performance is somewhat less than TiC.

2.3.3. HARD OVERLAY COATINGS:

Wear resistance is an important feature of this class of coatings. A number of methods are available for surface modification for improved tribological applications (Sundgren & Hentzell 1986). Plasma-assisted vapour deposition processes have also been promoted to produce wear-resistant coatings (Bunshah & Deshpandey 1986). Coatings of TiN, TiC and Ti(C,N) are used on tools, e.g. TiC on punching dies, thread guides, cemented carbide tool inserts, on steel ball bearings for use in severe conditions and on pistons and valves (Gass & Hintermann 1973). Ti(C,N) is deposited on carbon steel nailheads in an ultrasonic field (19 kHz at 15 W/cm_2) to improve adherence and toughness (Takahashi & Itoh 1979). Similarly, TiB_2 is deposited on Fe, giving an adherent 160 micron thick film (Takahashi & Itoh 1977). About 30% of the tool inserts used in the automobile industry are TiC coated (Schintlmeister & Pacher 1974, 1975). The TiC (4 to 8 microns thick) protects the Co binder. Its low thermal conduction gives a cooler tool and hotter chip. Its success is also due to its compatibility with the substrate (Hintermann 1972). In high speed cutting, the tool tip can reach 1500°C, where TiC and TiN oxidise and alpha alumina coatings are superior (Pollard & Woodward 1950;Yee 1978). The alumina is put on a TiC layer to improve its adhesion. A number of coating methods are available for wear applications including aqueous and molten salt deposition, as well as PVD and CVD methods.

Carbide Tools: TiC coated cemented tungsten carbide disposable inserts first appeared about 18 years ago, coated by CVD. Graded coatings like TiC-Ti(C+N)-TiN appeared later, offering life improvements of up to 10 times longer for continuous turning jobs. PVD TiC coatings are better than CVD TiC and are equal to CVD graded coatings (Bunshah 1978). PVD TiN coatings are better than CVD due to increased crack propagation resistance due to inherent porosity and to absence of the substrate embrittlement which occurs with CVD. TiN and TiC coatings are based on cobalt cemented WC-TiC-TaC tool tips (Peterson 1974). Coated tools show much lower forces during cutting, than uncoated tools.

High Speed Steel Tools: CVD often needs 1000°C which would cause softening of a high speed steel (HSS) tool. PVD requires only

450°C (which is below the steel tempering temperature). TiC coatings by the ARE process improves the life of HSS tools up to 8 times in continuous cutting, and tool forces are reduced 50% (Bunshah 1986,1978). Sputter TiN coatings on HSS tools give similar results. Life tests are needed for interrupted cutting mode tools such as end-mills, drills, reamers, etc.

Other Wear Applications: PVD hard coatings offer improved wear resistance to abrasive and adhesive wear and impact erosion wear. Sputtered WC-6Co and ARE-deposited TiC gave the necessary wear resistance to rotary bearing of Be and BeO in vacuum. Wear rates of PVD chromium carbide and nitride coatings on stainless steel were 4 to 8 times less than for electroplated hard Cr and 300 times less than for the uncoated substrate. TiC coated stainless steel wears 34 times better than electrolytic hard Cr plate currently used in industry (Bunshah 1978). A TiC coating is smoother than the rough electroless Ni, advantageous, e.g. in the textile industry. Impact erosion of quartz dust on stainless steel caused a mass loss whereas on a TiC coating there was no mass loss in the same conditions (Yamanaka & Inomoto 1982). Such hard coatings are needed for turbine fan blades subject to dust erosion. Ion plated Al_2O_3 deposits increase the wear resistance of stainless steel for coal gasification plant (Bunshah 1978).

Ni-Cr-B-Si alloys are used for hardfacing on tools and in the glass industry (Knotek & Lugscheider 1974). CVD TaC, 30 microns thick is used as a subterrene drill coating, able to withstand melting rock temperatures of 1350 to 2450K, in conditions of wear and corrosion (Stark et al 1974).

2.3.4. RUBBING SEALS:

Rubbing seals are used in ceramic regenerators in gas turbine engines; low leakage rates, corrosion and thermal shock, wear and fatigue resistance are the property requirements. Graphite and refractory metal dichalcogenides oxidise below 500°C and are thus unsuitable; ceramic and metal seals are in demand. 85% NiO + 15% CaF_2 or SrF_2 have been suggested (Moore & Ritter 1974) for their wear and corrosion resistance. Rubbing surfaces are also required in liquid metal cooled fast breeder reactors, able to resist wear, high temperature liquid metal (Na,230-650°C) corrosion and nuclear irradiation. WC spark coating 250 microns thick is economically produced by CVD with excellent adhesion but Cr_3C_2 was best in liquid Na at 200 - 625°C, among coatings tested (Johnson et al 1974). Studies of adhesion and effects of friction are lacking. Coatings of solid lubricants or inert barrier materials to prevent adhesion between a moving ceramic and a metal, are desirable, e.g. yttria. Laboratory research, rather than the much more expensive in-engine testing, would be very cost effective at the present stage (Lewis 1987).

2.3.5. THERMAL BARRIER COATINGS:

Thermal barrier coatings were first tested on a research engine in 1976. The current state-of-the-art coating system for gas turbine applications is a plasma-sprayed ZrO_2-(6%-8%)Y_2O_3 ceramic layer over an MCrAlY (M=Ni,Co or NiCo) bondcoat layer plasma sprayed at low pressure. However, the current coating concepts and plasma coating technology are as yet, inadequate to meet long-range needs (Miller 1987). Erosion and corrosion resistant thermal barrier coatings are very necessary for preventing overheating of metal parts in engines and some types of heat exchangers.

Poor adherence causing flaking has been a problem with some plasma sprayed coatings. The adhesion of plasma sprayed ceramic coatings to metals is generally poor but can be considerably improved if a sprayed bond-coat or interlayer is used e.g. NiAl or Mo. MgO-Al_2O_3-SiO_2 glass + powdered NiAl are applied on components exposed to vanadate containing fuels. $MgZrO_3$ thermal barrier coatings are used in turbine combustion chambers and yttria stabilised zirconia on turbine aerofoils (Freche & Ault,1976).

Thermal barrier coats reduce substrate air cooling requirements in gas turbine blades. An oxide acts as a thermal barrier, but oxides on MCrAl coatings are typically only 1 micron thick. To improve this, thermal barrier coatings are applied over existing coatings (Kear & Thompson 1980; Herman & Shankar 1987). This has been successful on gas turbine burner cans and exhaust liners. Yttria-stabilised zirconia plasma-sprayed layers 120-500 microns thick are used. To minimise thermal expansion stress the coatings are usually graded, changing gradually from substrate composition to ZrO_2, which is feasible by plasma spraying. Reductions of 100 degrees (C) in metal temperatures were achieved with 250 microns of yttria-stabilised zirconia over 100 microns of NiCrAl.

2.3.6. EROSION RESISTANT COATINGS:

Erosion resistant coatings are also needed for leading edges of gas turbine blades and pack cementation is used to give erosion and corrosion resistant aluminide coatings. Hard overlay coatings are needed for better protection, such as CVD Ti(C,N) on steel compressor blades (Wakefield et al 1974), using a thin Ni interlayer for better adhesion. Replacing the Ti(C,N) with CVD Cr_7C_3 gives much better thermal and mechanical shock resistance and also resistance to erosion, the latter ceramic being less brittle. Erosion of rocket nozzles is reduced by CVD coatings of Re, W and BC (Yee 1978) and pyrolytic carbon (Nickel 1974). NiCrAl/bentonite thermal spray powders for high temperature abradable seals have been tested (Clegg & Mehta 1988).

2.3.7. DIFFUSION BARRIER COATINGS:

TiC is used as a carbon diffusion barrier for Ta coatings on steel and TiN is a nitrogen diffusion barrier coating on SiC heating elements. Barrier coatings on metals prevent inward (and outward) C diffusion (carburization and decarburization), important for AGCR-s. TiC barrier coatings on BC particles dispersed in a W-Co matrix, prevent the BC reacting with the matrix during hot presssing at 1350°C. Diffusion barriers are used on fibre-reinforced materials; B, SiC, C, W fibres in metals interact (during hot pressing fabrication or high temperature use) causing embrittlement, loss of strength of the fibres and adverse effects on the metal structures. Development of diffusion barrier coatings is an important research area. Application is being delayed. The thermodynamics of interfaces between metals and ceramics is discussed in terms of surface energies and heats of formation of alloys (Wynblat & McCune 1980). Thus Pt alloying with Al explains why Pt reacts with alumina and the Pt surface absorbs 7% Al at 1527°C in H_2. This is known as 'solid state reaction bonding' and the bond remains durable even after long times at high temperatures. At magnifications of over 100000 an intermediate liquid phase is seen which wets the ceramics, and not recrystallising on cooling; the bond mechanism is not understood (Bailey & Borbidge 1980).

In older methods of metal-to-ceramic bonding, brazing is used in which a liquid metal or glass filler wets the ceramic to form the bond; this is limited to the few metals that will wet ceramics, e.g. Ti alloys. Metallizing ceramic surfaces prior to electroplating or brazing, involves Ag or Au alloys. Reducing or inert gases are needed throughout. The main limitation is the restricted temperature range for use of such bonds. Reaction bonding is a high pressure solid state process to join metals to ceramics (Allen & Borbidge 1983). Noble and transition metals can be bonded to Al_2O_3, MgO, ZrO_2, SiO_2 and BeO_2, for example. Such bonds retain their strength at high temperatures and breakage under load is often in the ceramic and not at the bond site. Solid state reaction bonding is performed at about 90% of the m.p. of the lowest component, usually in air, with a light clamping action for times between a few seconds and about 3 hours; the ceramic surface is polished to optical flatness for maximum bond strength. Pt has an expansion coefficient similar to that of most ceramics. Ni is suitable in inert atmospheres and bonding is due to a spinel, $NiO-Al_2O_3$.

2.3.8. CERAMIC COATINGS ON CERAMICS:

ZrN whiskers deposited on quartz tubes give a superhard surface (Motojima et al 1979). Si_3N_4 can be deposited on sintered vitreous silica by CVD at 800 to 1200°C (Mellottee et al 1976). TiB_2 can be deposited on uncoated and Ti-coated WC for tool tips by CVD (Zeman et al 1982). Si_3N_4 coatings on graphite, alumina, BN, SiO_2 and hot-pressed Si_3N_4 are deposited by CVD (Galasso et al 1978). Si_3N_4 on graphite is used as rocket nozzles or high temperature blades. An inner SiC layer and an outer glaze based on B_2O_3, P_2O_5 or SiO_2 have been tried on carbon-carbon composites (Strife & Sheehan 1988). BP CVD coatings on Si,Mo,WC and C have been little researched. BP is very refractory and hard (Morojima 1979). Polycrystalline Si coatings on graphite susceptors give oxidation resistance (Van den Brekel 1977).

TiZrB coatings are used on graphite, giving good mechanical shock resistance, high hardness and melting point (Takahashi & Kamiya 1977). ZrC-C coatings on semicircular graphite/Mo are used as fission product barriers in gas cooled nuclear reactors (Ogawa et al 1979). Low cost refractory crucibles for metal melting are lined with a coating inert to the molten metal. A selected few are listed in Table 2:3.

Coatings protect resistance heating elements, e.g. SiC coated graphite, SiO_2 coated SiC. For molten metal probes, 2-layer ceramic coatings are used - a porous thermal shock resistant layer over a dense chemically resistant layer (Nat. Acad. Sci. Rep.1970).

TABLE 2:3

REFRACTORY LINING COATINGS TO GRAPHITE

Lining	Melt
AlN	Al
AlN + SiC	Al
alumina	Al, Ni, Co, Fe
clay	Fe, Al
$MgZrO_3$	U
mullite	Al
thoria	most metals
TiN, ZrN	Co, Fe
zirconia	Ru, Rh, Cr

2.3.9. DESIRABLE CERAMIC COATING PROPERTIES:

Elasticity in a ceramic coating is desirable to combat thermal cycling spalling. The elasticity of ceramics increases with porosity, but porosity is bad for corrosion. Fig.2-6 (Perugini 1976) shows the balance of these two effects. Fig.2-7 shows how self-sealing ceramic coatings offer a solution since their surface layer presents a closed porosity to the gas or other corrodent. The as-sprayed coating has an open porosity but this is closed by

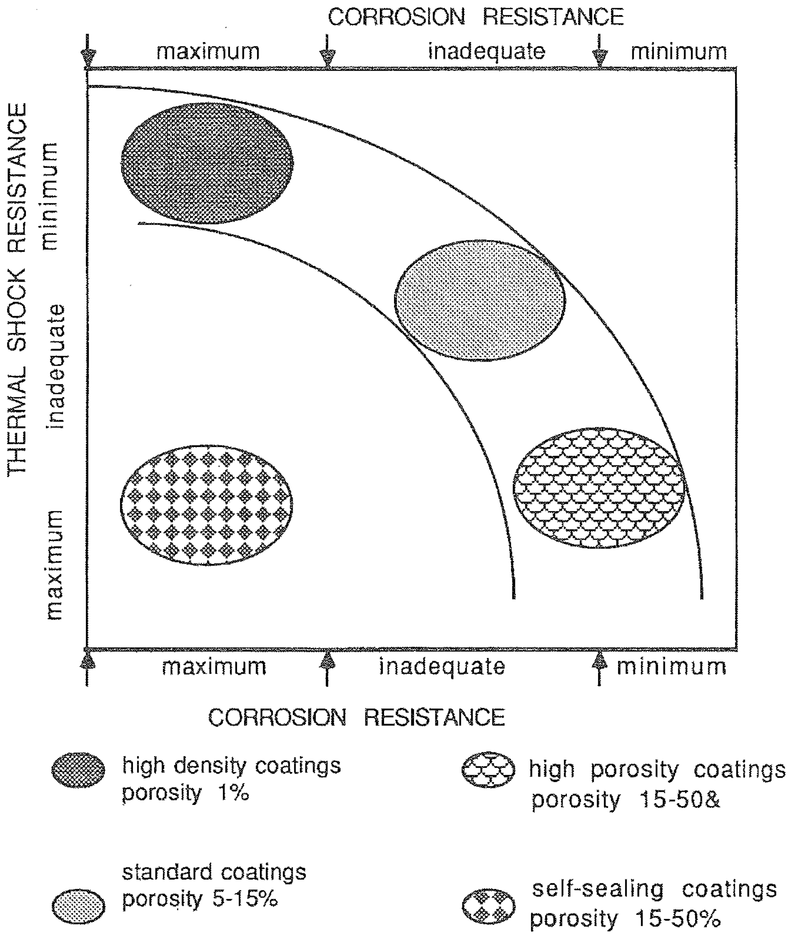


Fig.2-6: Effect of Coating Porosity on Resistance to Thermal Shock and Corrosion

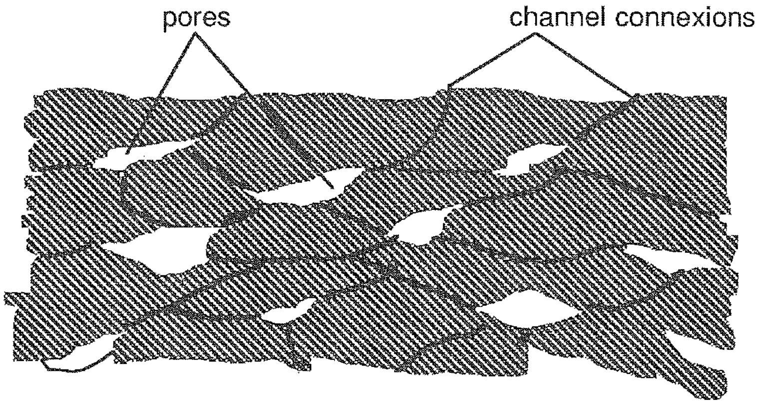


Fig.2-7: Porous Structure of Self-Sealing Coatings

(Perugini 1976)

topochemical reactions (Perugini 1976). A graded bond to the metal is essential, e.g. Ni or Ni alloy (m.p.800 to 1350°C) forms a metal bond to the metallic substrate, Cr on top bonds to the Ni and by oxidising also seals the inter-pore channels in the ceramic above. Between the Cr and the ceramic a thin layer of stabilized zirconia (for example) is used. Thermal conductivity and heat capacity decrease from inner to outer layer while elastic modulus and melting point increase. The inner and second layers may include the third as a cermet. The self-sealing effect also confers the ability to heal cracks. Tensile and shear strengths >3kg/mm^2 and bending angles of 5° without detachment are reported (Perugini 1976).

2.4. COMPOSITE COATING SYSTEMS

Composite coatings may be made up of two or more individual and/or single coating materials, either in a layer-mode or mixed mode. A special category of the mixed mode is termed a cermet, meaning that it is made up of a ceramic and a metal. Cermet coatings combine the heat resistance and strength of ceramics with the ductility and thermal conductivity of metals. Particle and fibre-reinforced composites are currently being investigated to identify those which can incorporate ceramics with a negative coefficient of thermal expansion (Chu et al 1987). Composite production in powder form and mechanical alloying has progressed rapidly. Rapid solidification processing - RSP (Das & Davis 1988; Wadsworth et al 1988; Hays & Harris 1987; 6th Inter-Nat. Conf. Proc. 1987 in Mat. Sci. Eng. Vol. 97-99, 1987; Panitz 1986; Kear & Gissen 1984) and mechanical alloy processing (MAP) are two proven new methods for special alloy and cermet production.

Cermet coated enamelling steel is good up to 600°C under thermal cycling, but rigid quality control is needed during coating. Life is longer than for Al coatings and no brittle intermetallics form. Cermet coated steels are not yet recommended for gas flues and further research is needed. Cermet oxy-acetylene flame sprayed coatings of Ni+5% Al+30% alumina on steel give good oxidation protection with excellent thermal shock and cycling resistance, in gas fired applications. A rough surface gives better heat transfer and this feature may simplify heat exchanger design. For solar power units, coatings are used on stainless steels and superalloys and resist daily thermal cycling and thermal gradients. Absorbing coatings (black) are essential for this purpose, e.g. oxidised Cr, Ni and Co (Perkins 1981).

Multilayer films can give selective solar absorption by interference effects but are expensive and unstable due to high temperature interdiffusion (Mattox & Sowell 1974). For nuclear fusion reactors, coatings will be used for first wall armour and limiters. Suitable low neutron capture coatings are borides (TiB_2, VB_{12}), carbides (B_4C, TiC, SiC) and elements (B, C, Be). For fission reactors coatings are used for HTGR heat exchangers. Suitable contamination control coatings are Cr_3C_2, $Cr_{23}C_6$ + NiCr. These can be produced by CVD, PVD, sputtering, plasma spray and detonation gun (D-Gun) (Perkins 1981; Lewis 1987).

Electrodeposition of TaC is the first successful electrolytic coating of a refractory carbide from a high temperature electrolyte (Stern & Gadomski 1983) and offers promise for the coating of complex shapes. Further research to develop this is important. Studies of the mechanism of carbonate reduction in fluoride melts and of simultaneous reduction to Ta and C would give a better understanding of the coating composition. A dispersion of Al_2O_3 or TiO_2 in a metal confers a high resistance to recrystallization and grain growth, thus retarding loss of hot strength (Greco & Baldauf 1968; Sautter 1963).

SiO_2, Al_2O_3, TiO_2, ZrO_2, SiC, WC, BC, diamond and glass powder have all been codeposited from aqueous electrolytes, e.g. with Ni from a Watts electroplating bath. These coatings have wear resistant properties. ZrB in Cr gives oxidation resistance. Wear resistance is due to the presence of hard particles and also to the dispersion hardening of the matrix, which however still retains some ductility so that the coatings have both ductility and toughness (Pushparaman et al 1974). Electrodeposited cermet-coated steels have been successful in prolonging the service life of hot risers in sour gas wells (Hocking et al, 1984; Report, Ind. Corrosion 1987). Cermets have also been electrodeposited for well-proven application in gas turbine systems (Kedward et al 1987).

2.5. AMORPHOUS COATINGS

Certain groups of alloys with well characterized crystal structure and metallic properties can be rendered amorphous in structure but yet retain much of their metallic properties when they are subjected to rapid solidification from their molten state. They were first called metallic glasses in the early seventies, but in coating and powder production areas the terminology is less used and replaced by amorphous metals or rapidly solidified products (RSP). The materials are of interest in the field of coatings because of their remarkably high corrosion resistance and wear characteristics. Laser-oriented coating processes and powder metallurgy technology have enabled the exploration of this class of coating systems together with cermets.

Amorphous alloy films were first produced in the 1950s (Buckel & Hilsch 1954). Using quench techniques capable of achieving cooling rates of the order of 10^6 K/s the process of nucleation and crystalline phases could be kinetically by-passed to yield a frozen alloy melt - metallic glass (Duwez etal 1960, 1966; Turnbull 1961). The material has been deposited from the vapour phase by PVD and CVD techniques, while melt spinning, splat cooling and liquid atomization adopt the liquid quench approach. Atomization is a fast-developing powder metallurgy technique. Early production of amorphous alloys was mainly in the form of 2-3 mm wide ribbons. But since the development of powder metallurgy and laser techniques, amorphous alloys are a new class of high temperature material and coating system poised to move onto further development (Johnson 1986).

Table 2:4 gives a summary of coating systems studied for high temperature materials.

TABLE 2:4

HIGH TEMPERATURE SUBSTRATES - TYPES OF COATINGS USED

Substrates	Coatings
Fe-, Ni- & Co-base alloys	Al, Cr, Si; MCrAlX (M = Fe and or Ni and or Co; X = Y,Hf,Ce,Zr,Ti,Ta etc. with variations).
	Cermets: Co-Cr_2C_3; Ni- and or Co- with ceramics - Al_2O_3 etc.
	Ceramics - a number of oxides, carbides, borides and nitrides
	Platinides; other refractory metal depositions.
	Surface modification by various PVD, CVD and Laser methods.
Refractory metals - Nb, Ta, W, Mo & Cr	Silicide coatings: Si -Mo, -Nb, -Cr-Ti, -Al-Cr with Al, B, Cr, Ti and V additions.
	Aluminide coatings: Al -Nb, Ta, Ni with Cr, Si, Sn and Ti additions.
	Beryllide coatings: Be -Ta, -Ti, -Nb, -Cr, -Mo and Zr.
	Others: Nb-Zn
Graphites	Ir, SiC, oxides - HfO_2, ThO_2, Zr_2, borides - HfB_2, ZrB_2

2.6. COATING PROCESSES

This section gives a general introduction to a number of physical and chemical coating processes available and the several categorization of the coatings and coating methods. Chapters 3-6 cover the processes in greater detail.

2.6.1. GENERAL:

Almost all the processes given can be adapted for producing thick or thin films. In distinguishing coating parameters the demarkation of thin or thick films is often ambiguous. 10000 Angstrom (10^{-3}mm) is more or less accepted as the boundary between them. Another viewpoint is that a film can be considered thick or thin depending on whether it exhibits surface-like or bulk-like properties (Perkins 1981). Various units appear in coatings literature, viz. 1 mil = 0.001 in. = 25.4 micron; micron 1 = 1 micrometre = 10^{-3} mm. Coating performance is not necessarily pro-rata to its thickness nor entirely ascribable to the coating composition. It is difficult to specify a critical threshold on the basis of the coating material itself because it is not a standalone parameter. Each coating has to be assessed in conjunction with the substrate and the environment.

A thickness criterion for a coating is subjective. The same process can be adapted to produce opaque or transparent coatings and films. Most of the coatings considered for power and energy applications are opaque. Their hardness, corrosion resistance together with their compatibility to substrate service-conditions for physico- and chemico- mechanical and -thermal responses are the deciding factors. Hard, insulating and optically transparent films, on the other hand, have various other applications in metallurgy, surface finishing, semi-conductor, and optical industries. Their physical properties are very high hardness (up to 6000 Kg/mm^2 VHN), low coefficient of friction (0.04 - 0.08 steel/steel), corrosion resistance, chemical inertness, high resistivity (10^{12} ohm.cm), and the infrared refractive index (2 for carbon).

2.6.2. COATINGS & COATING PROCESS CLASSIFICATION:

Several ways of classification are reported in literature. Table 2:5 shows a categorization on the basis of a solid, liquid, gas and plasma media of matter from which the coating material is obtained. Table 2:6 gives a further breakdown of the material state and medium - that the coating is obtained from various particle states - atomic, ionic, bulk - micro-, macro-, and structure modified states. Some of the processes are carried out in a variety of routes; these are given in table 2:7. Some of the well known general features of coating processes are indicated in table 2:8 (Biswas 1986; Chatterji et al 1976; Nat. Acad.

Sci. Rep. 1970).

Pack cementation was one of the first and cheapest high temperature coating processes to be developed for aluminiding and chromizing individually or together. Table 2:9 gives a comparative rating for it regarding process costs and Table 2:10 gives the current status of a number of diffusion aluminiding coating processes (Nicholls & Hancock 1987; EUR 1982). Superalloy coating processes are surveyed in Table 2.11.

TABLE 2:5

COATING METHODS SHOWN BELOW COATING MEDIA AVAILABLE

Solid state	Liquid State	Semi-liquid or Paste	Gaseous State (atomic/ionic/ electron interaction)	Dissolved Solutions	Plasma
Bonding	Hot Dipping	Sol-Gel	PVD	Chemical	
Cladding	Spraying	Slurry	CVD	Galvanic	
Sintering	Welding	Brazing		Electro-galvanic	
	Surfacing				

TABLE 2:6

COATING PRODUCTION PROCESSES: CATEGORISATION BY MATERIAL STATE & FABRICATION ROUTES

Group 1 Atomic/Ionic State	Group 2 Macro Particle State	Group 3 Bulk Material State	Group 4 Structure Modified State
Vacuum Medium Vacuum Evaporation Ion Beam Deposition Molecular Beam Epitaxy	Impact Coating Fusion Coating Thick Film Inking Enamelling Electrophoretic	Overlaying Weld coating Cladding Explosive- Roll Bonding	Laser Surface Modification (LSM) Thermal Treatment Ion Implantation
Plasma Medium Sputter Deposition (Ion; Magnetron) Ion Plating Plasma Polymerization Activated Reactive Evaporation Cathodic Arc Deposition	Thermal Coating Flame Spraying Plasma Spraying Detonation Gun (D-Gun) Spraying	Laser Melting Wetting Method Painting Dip Coating	Surface Enrichment Diffusion from Bulk Sputtering
Chemical Vapour Medium Chemical- Vapour Deposition Reduction Decomposition Plasma Enhanced Spray Pyrolysis	Sol-Gel Medium	Electrostatic Method Spin Coating Spray Printing	Leaching Chemical- Conversion Liquid Vapour (Thermal, Plasma) Diffusion
Electrolyte Medium Electroplating Electroless Plating Molten Salt Electrolysis Chemical Displacement			Electrolytic- Anodization Molten Salt Heat Treatment Mechanical Method Shot Peening

TABLE 2:7

TYPE CATEGORIZATION OF COATING PROCESSES

Mechanical	Physical	Chemical	Electro-chemical	Spraying	Welding
Cladding	Vapour deposition	Vapour deposition	Aqueous	Detonation gun	Laser
Bonding	(PVD)	(CVD)	Molten salt	Electric arc	Manual Metal Arc (MMA)
	Vacuum coating;	Electroless			Metal Inert Gas (MIG)
				Metallising	Oxy-Acetylene
	Thermal evaporation			Plasma	Plasma tranfered arc
	Sputtering			Flame-Powder Wire	Plasma welding
	Ion Plating				Spray fusion
					Submerged arc
					Tungsten inert arc (TIG)

Two Other Methods:- (no alternate techniques which can be categorised individually):

Ion Implantation & Hot Dipping

TABLE 2:8

GENERAL SURVEY OF COATING PROCESS CAPABILITY & DRAWBACKS

Method	Capability	Drawbacks
Physical Vapour Deposition (PVD)	Versatile; all solid elements, and materials can be deposited. Thin films and reasonably thick coatings are possible. Several variations in technique. * 5-260 microns.	Operations are mostly line-of-sight. Poor throwing power. Equipment expensive.
Chemical Vapour Deposition (CVD)	Competitive to PVD; elements & compounds chemically reactive & in vaporized state are coated. Good throwing power. * 5-260 μm	Heat sources play an important role. Generally operates at higher temperatures than PVD. Substrate overheating possible. Undesirable directional depositions possible.
Cementation	Good uniformity & close dimensional tolerance. A very cost-effective process. Most coated materials - Al & Cr. Hard depsits. * 5-80 microns	Substrate size a limitation. Not for high temperature-sensitive substrates.Thinner films than other diffusion processes. Coating embrittlement possible.
Spraying	Technique & starting material controlled process. Thick & uniform coverage possible. * 75-400 microns	Skilled operator dependent. Substrates have to be heat- and impact tolerant. Porous & rough coatings with possible inclusions unless controlled.
Cladding	Thick coatings possible. Large substrates can be handled. * 5-10% of substrate thickness.	Substrate distortion possible. Suitable for robust substrates.
Electro-deposition (also electroless; electrophoresis)	Cost-effective aqueous process. Fused salt electrolytes yield precious metal and refractory deposits. Cermet production in industrial use. Electroless & electrophoresis are limited to a few elements and substrate sizes. *0.25 - 250 microns	Good plant design to ensure good throwing power. Molten salt electrolytes require rigorous control to prevent moisture ingress & oxidation. Melt evaporation a problem. Coatings can be porous & under stress. Limited to specialised areas in high temperature.
Hot dipping	Relatively thick coatings. Fast coating method.* 25-130 microns.	Limited to Al for high temper-ture applications. Coating can porous and discontinuous.

*Coating Thickness

TABLE 2:9

PACK COATING : PROCESS STATUS & COSTS

Process	Availability	Relative Cost
Pack aluminising	Widely used coating with lowest unit cost. Euipment can be installed at moderate capital cost, enabling facilities to be available throughout the world.	1
Chromium- or Cr-Ta-modified aluminising	Equipment similar to that for pack aluminising. Process available in Europe and America.	2-3
Platinum-modified aluminising	Equipment similar to that for pack aluminising, plus special facilities for Pt-electroplating from fused salts. Process available in Europe and America.	3-5
Vapour-deposited overlay coatings	Sophisticated vacuum equipment and analytical control facilities required, therefore very high plant cost. Production capability available mostly in the U.S.A. Branches of US firms in UK. Limited facilities in France, Germany, Sweden and Switzerland, and independently in USSR.	7-10

TABLE 2:10

DIFFUSION ALUMINIDING COATING PROCESSES & THEIR CURRENT STATUS

Process Route	Coating Designation & Manufacturers	Process Status
PackAluminizing - Low & High Activity	Proprietary names - Gas turbine manufacturers and individual firms.	Active industrial
Pt- electroplated coating + Pack Aluminizing	LDC2/manuf. TEW; RT22/manuf. Chromalloy	Active industrial
Pt- metalliding from fused salts + Pack Aluminizing	JML1 & JML2/ manuf. Johnson Matthey	Engine Trials
Pack Chromizing	PWA70 (also HC12;MDC3V; RT5.A_1 etc.)/several manufacturers	Active industrial
Pack- co-deposited Aluminizing & Chromizing	HI 15/manuf. Alloy Surfaces	Laboratory & Burner rig tests
2-step Pack Chromizing + Aluminizing (some with siliconizing - SiO_2 safer than Si)	PWA62 (also HI32;RT17; SylCrAl & others)	Active industrial
Ta coating + Pack Aluminizing & Chromizing	Tan CrAl	-- as above --
Si/Ti Slurry Diffusion	Elcoat 360/Elbar	-- as above --
Al/Si Slurry diffusion	Sermaloy J/Sermetal	Burner rig tests

(Nicholls & Hancock 1987)

TABLE 2:11

KEY COATING PROCESSES FOR SUPERALLOYS: A BRIEF SURVEY

Process	Number of Steps	Environment	Comments
Pack Cementation (also halogen Streaming and slip pack methods) Al, Cr, Al-Cr, Al-Cr-X (also Be)	Normally single pack; could be two or more as required.	Inert to start with; vacuum in some systems. Reacting medium, eg.chloride is supplied when pack reaches required temperature.	Slip-pack process requires components to be supported. Special holding fixtures when used, cause blind spots in coating. Regular pack process eliminates this. Disadvantage: long heating and cooling times.
Slurry Al, Cr, Al-Cr, Al-Cr-X	Multiple	Heating cycle uses both inert and vacuum atmosphere. Slurry application in vacuum yields good coverage.	No heating and cooling cycles, but special holding fixtures are needed. (blind spots in coatings).
Physical Vapour Deposition (PVD): Al, Cr, Si, and a large range of alloys.	Normally two.	Pumped down to vacuum.	Sophisticated and expensive. Poor throwing power; not readily repairable. Allows versatile combination of elements.
Chemical Vapour Deposition (CVD): Al, Cr; technical limitation - none.	As for PVD	Vacuum as for PVD; inert gas also used.	Compares with pack cementation. Requires holding fixtures. Can yield undesirable directional deposition.
Fused Salt Electrolysis Electrolytic; electroless: a number of refractory metals, and rare earths.	One or two. Multi-component systems need additional steps.	Inert gas cover; moisture avoidance very important.	Limited to small components. Difficult and expensive to maintain; can be toxic and and hazardous. But enables 'hi-tech' coating.
Vitreous Enamelling (glassy-bonded refractory)	Generally multiple	Selective: air or inert.	Yield brittle coatings; relatively thick gauge. Limited to about 1000°C in service.
Hot-dipping Al, Al-X	Generally multiple	Presence of flux or inert.	Short process times. Scope limited.
Electrophoresis Al-rich	Multiple	Dielectric organic solvent.	Limited to relatively small components.

2.7. LIST OF ACRONYMS

Acronyms found in the literature of deposition processes, techniques, analyses and applications are cited here. New words and letters get introduced at a fast rate. The list, therefore, is not exhaustive. Acronyms are used for brevity, and should be 'coined' with care to avoid ambiguity, absurdity or sometimes serious errors. C2S (di-calcium silicate), C3S(tri-calcium silicate), C3A (tri-calcium aluminate), C4AF (tetra-calcium alumino ferrite) etc., by civil engineers to express chemical formulae are a few examples of such use. A more serious error occurs if a chemical formula is allowed as abbreviation; for instance, CO for Cr_2O_3; the authors report on mechanical testing of plasma sprayed coating of chromic oxide on cast iron (Colin et al 1988).

Coating, Deposition, & Plating

CVD - Chemical Vapour Deposition
CCVD - Conventional CVD
LCVD - Laser CVD
LACVD - Laser Assisted CVD
LECVD - Laser Enhanced CVD
LPCVD - Low Pressure CVD
MFCVD - Molecular Flow CVD
MOCVD - Metal Organic CVD
MPCVD - Magnetron Plasma (enhanced) CVD
IHPACVD - Induction Heated PACVD
PACVD - Plasma Assisted CVD
PECVD - Plasma Enhanced CVD
RPECVD - Remote PECVD

CVI/CVD - Chemical Vapour Impregnated CVD &/or
- Chemical Vapour Infiltration CVD

CCRS - Controlled Composition Reaction Sintering
HTLA - High Temperature Low Activity (Pack process)
LTHA - Low Temperature High Activity (Pack process)
PPP - Pressure Pulse Pack

AVID - Arc Vapour Ion Deposition
CAPD - Cathode Arc Plasma Deposition
EBPVD - Electron Beam PVD
ESD - Electro Spark Deposition
PVD - Physical Vapour Deposition
PAPVD - Plasma Assisted PVD
RPAPVD - Reactive Plasma Assisted PVD

IAC - Ion-assisted Coatings
IAD - Ion-Assisted Deposition
IBAD - Ion Beam Assisted Deposition
IBED - Ion Beam Enhanced Deposition
IVD - Ion Vapour Deposition

RE - Reactive Evaporation
ARE - Activated Reactive Evaporation
BARE - Biased ARE
PARE - Plasma ARE
RSAE - Random & Steered Arc Evaporation

RS - Reactive Sputtering
(also used for Raman Spectroscopy)

CIP - Cathode Ion Plating
IAC - Ion Assisted Coating
IP - Ion Plating
SIP - Sputter Ion Plating
RIP - Reactive Ion Plating
RTIP - Reactive Triode Ion Plating

HHC - Hot Hollow Cathode
HCD - Hollow Cathode Discharge
ICB - Ionized Cluster Beam (Process Technique)

LPAS - Low Pressure Arc Spray (-ing)
LPPS - Low Pressure Plasma Spray
RPS - Reduced Pressure Plasma Spray
SPS - Shrouded Plasma Spray
UPS - Underwater Plasma Spray
VPS - Vacuum Plasma Spray

Laser Process

LASER - Light Amplified Stimulated Emission Radiation
cw or CW - Continuous wave
Nd YAG - Neodymium Yttrium Aluminium Garnet
TEA - Transversely Excited Atmospheric (laser)
LW - Laser Welding
LAPP - Laser Physical Properties
LSA - Laser Surface Alloying
LASAP - Laser Surface Alloying Parameter
LST - Laser Surface Treatment
LSM - Laser Surface Melting
LAZ - Laser Affected Zone
LACVD - Laser Asssisted Chemical Vapour Deposition
LECVD - Laser Enhanced Chemical Vapour Deposition
LAPVD - Laser Assisted Physical Vapour Deposition
LAPC - Laser Assisted Plasma Coating

RSP - Rapid Solidification Processing

Analyses: Microscopy, Spectroscopy

AEM - Analytical Electron Microscopy
AES - Auger Electron Spectroscopy
ATIS - Automatic Thermal Impedance Scanning

EASE - Electron(ic) Absorption Spectroscopy Experiments
EELS - Electron Energy Loss Spectroscopy
ETM - Electron Tunnelling Microscopy
EDAX - Electron Dispersive X-ray Analysis
EDX - as above
EPMA - Electron Probe Microanalysis
ESCA - Electron Scattered Chemical Analysis
GDMS - Glow Discharge Mass Spectroscopy
MS - Mass Spectroscopy
OES - Optical Emission Spectroscopy
ISS - Ion Scattering Spectroscopy
NMR - Nuclear Magnetic Resonance
PMS - Plasma MS
RS - Raman Spectroscopy (to note context in text)
RBS - Rutherford Backscattering Spectroscopy
SIMS - Secondary Ion MS
SAM - Scanning Auger Microscopy
SEE - Secondary Electron Emission
SEM - Scanning Electron Microscopy
SXS - Soft X-ray Spectroscopy
STEM - Scanning Transmission Electron Microscopy
STM - Scanning Tunnelling Microscopy
TEM - Transmission Electron Microscopy
UPS - Ultraviolet Photoemission Spectroscopy
WDX - Wave Dispersive X-ray analysis
XPS - X-ray Photo-Spectroscopy
XRD - X-Ray Diffraction

Miscellaneous

ac/AC - Alternating Current
AFBC - Advanced fluidized-bed Combustion
AGR - Advanced Gas (cooled) Reactor
AGCR - Advanced Gas Cooled Reactor
DBTT - Ductile Brittle Tranformation Temperature
dc/DC - Direct Current
DRM - Dynamic Recoil Mixing
DS - Directionally Solidified (alloys, superalloys etc.)
EDCC - Electro-Deposited Composite Coating
EXAFS - Extended X-ray Absorption Fine Structure
FET - Field Effect Transistor
HCD - Hollow Cathode Discharge
HSS - High Speed Steel
HTGR - High Temperature Gas (cooled) Reactor
IH - Induction Heating
ODS - Oxide Dispersion Strengthened (alloys, products etc.)
MAP - Mechanically Alloyed Products
MMC - Metal Matrix Composites
MNS - Metal-Nitride Silicon (devices)
MIOS - Metal Insulator Oxide Silicon (devices)
NDE - Non-Destructive Evaluation
NDT - Non-Destructive Testing
PFBC - Pressurized Fluidized-bed Combustion

PM	- Powder Metallurgy (components, products etc.)
rf/RF	- Radio Frequency
RSP	- Rapid Solidification Processing
SCC	- Stress Corrosion Cracking
TESS	- Tribologically Engineered Surface Selection
UHV	- Ultra High Vacuum
VHN	- Vickers Hardness Number
VLSI	- Very Large Scale Integrated Circuits

CHAPTER 6

Coatings by laser surface treatment, rapid solidifications processing, spraying, welding, cladding and diffusion methods

6.1. IN THIS CHAPTER

Six coating methods are dealt with in this chapter, all of which are individual process methods, but are also more often used in conjunction. Diffusion is an inevitable surface/coating phenomenon except where diffusion barrier overlayers are applied, and a number of coating methods involve one or more post-coating heat treatment step wherein diffusion is the means for coating consolidation or modification of its morphology . Diffusion bonding (DB) as a coating method in its own right is discussed in this chapter. Cladding is self-explanatory. Welding has been a traditional 'cementing' or joining technique which has in recent years advanced rapidly as a surfacing technique. Both cladding and welding are classified as bulk-surfacing methods. The former uses the material to be coated in a solid form while solid and molten media in bulk are encountered in welding. Coating by droplet transfer using plasma-, arc- or detonation-gun (D-Gun) spraying is another form of bulk-coating method, with the material to be coated in a liquid or slurry form. Rapid cooling of molten alloys results in amorphous or 'vitreous' structures and the materials solidified thus exhibit high resistance to wear and corrosion. Rapid solidification processing (RSP) is a fast-developing coating technology. The laser has proved a very versatile processing tool to perform well-controlled, small area surfacing, welding, cladding, spraying and rapid solidification processes. This technique is covered at the outset in this chapter.

6.2. LASER COATING TECHNOLOGY

The application of lasers in coating technology has developed rapidly since 1980 although the first attempt at laser surface alloying was reported in 1964 (Cunningham 1964). Laser cladding by powder fusion progressed from research to development during 1974 to 1978 (Powell & Steen 1981). Now lasers are used as one of the main means of application of coatings, as a manipulated auxiliary in other depositon processes such as CVD, and PVD techniques, as well as in a number of surface modifying methods such as cladding, welding and spraying. The practical utility of lasers has stretched far beyond the area of coating technology itself.

A concise list of literature sources is appended to provide most of the preliminary information on the use of lasers in both thin film and bulk coating methods. They also provide a broad spectrum of the use of lasers in surface modification welding, drilling, cutting, machining and non-destructive testing of a number of metals and alloys: (Ferris et al 1979; White & Peercy 1980; Gibbons et al 1981; Bahun & Engquist 1964; Mukherjee & Mazumder 1981; Metzbower 1979; Draper & Mazzoldi 1986). The compatibility of lasers to refractories and cermets are undefined, although Kelly has succeeded partially in welding ODS-type Ni-base alloys (1979). Abbreviations very typical of laser processes are listed in the Acronyms section (Chapter 2; section 2.7.).

6.2.1. LASER CHARACTERISTICS

The laser is a singular source of heat produced by means of highly energetic, coherent, monochromatic beam of photons which can be manipulated to operate in focused or defocused states. It is capable of attaining very rapid rates of heating, and is clean, intense and localized. It can be produced either in a continuous form or pulsed. A laser beam incident on a substrate can heat, melt, vaporize or produce plasma depending on the manipulation of the controlling parameters. The principal sections of a laser are given in Table 6:1 and Fig.6-1 (Bass 1979). The overall portability and efficiency of the equipment and its repair and maintenance costs have to be considered in its eventual selection for use.

The main characteristics of the lasers utilized in LSA processing are given in Table 6:2 (Draper 1981). The wider application of lasers became possible when multi-kilowatt CO_2 lasers came into production in 1970. Now CW CO_2 lasers are available from a few watts to many kilowatts power; a CW Nd YAG laser of 400W is also in production.

6.2.2.

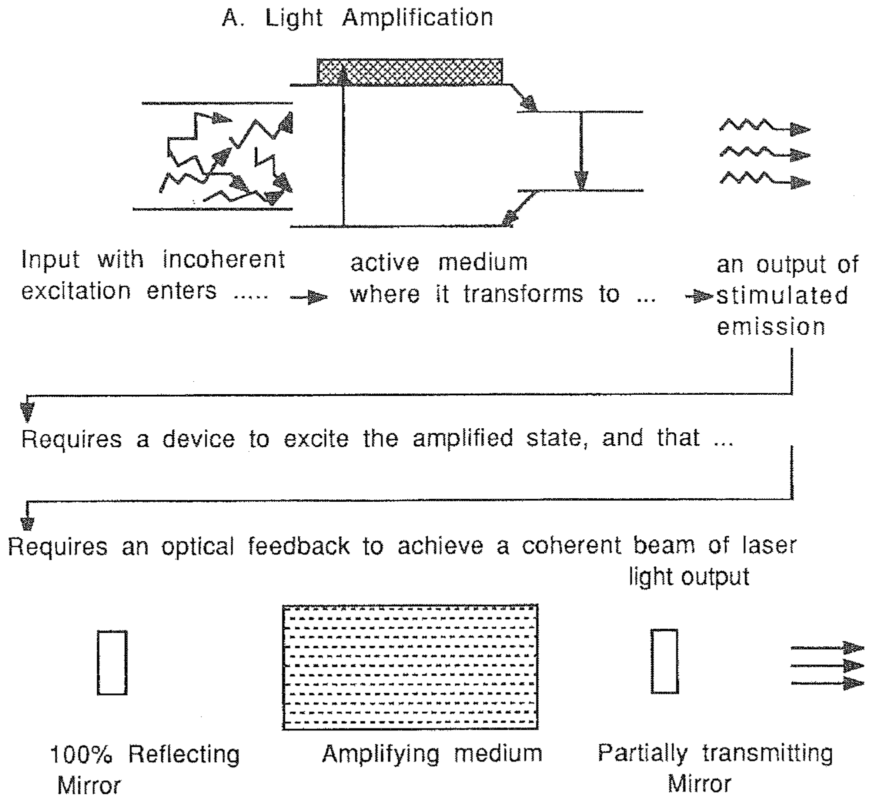


Fig.6-1: Features of a Laser Device

TABLE 6:1

PRINCIPAL SECTIONS OF A LASER

Section	Factors in Design
Amplification of Light	Optical quality; Types of windows; Means of heat removal; Repair and efficency; Cost.
Excitation	Power supply: I stage amplifying state auxiliary supply for cooling, pumps etc; Weight, Performance, Efficiency; Cost.
Optical Feedback System	Reflector components: Mirrors, lenses, coatings modulators; windows; Mechanical and optical stability.

TABLE 6:2

LASER CHARACTERISTICS

Laser Source	Laser Wavelength (microns)	Power Output (W)	Log (Time, sec.) (Dwell or Pulse Time)	Repetition Rate, Hz
Continuous CO_2	10.6	500-20K	-1 to -5	cw
Pulsed Nd-YAG	1.06	200^	-2 to -3	100
Pulsed Nd-glass	1.06	10^6*	-2 to -3	1
Pulsed Ruby	0.69	10^6*	-2 to -3	0.2
Q-switched Nd-YAG	1.06 0.53	1^	-6.75^	$10^3 - 5 \times 10^4$
Q-switched Ruby	0.69	10^8*	-8.7 to -7.7	2

* peak value ^ average value

6.2.3. LASER SURFACE TREATMENT (LST)

Laser surface treatment can be controlled to achieve alloying, cladding, grain refining or transformation hardening a metal surface without actually affecting the bulk of the metal itself. This is mainly due to the localized nature of laser heating. LST can be categorized into three main sections and its various effects on a substrate may be shown as in Fig. 6-2 (Gnanamuthu 1979).

Fig. 6-2

Effects of Application of Laser Power on Materials

```
                                 ---> Annealing
                 --> Heating
                                 ---> Trans. hardening


                                 ---> Alloying
                                 ---> Cladding
   Laser Power --> Melting
                                 ---> Glazing
                                 ---> Grain refining

                 --> Shocking ------>Shock hardening
```

A laser beam can enchance surface properties to a controlled, confined extent depending on the power and dwell time of the beam and the thermal characteristics i.e. heating and cooling, of the surface treated (Table 6:3). Surface treatment prospects by lasers were observed with pulsed lasers at first. A laser can be a giant-scale spot welder of one surface to another with very little seal or dilution zone, or it can cause good mixing of the substrate metal with the top coat to yield an alloy. Being inertialess, it has high processing speeds with very rapid stop and start facility. Q-switched laser processing offers quenching rates of 10^{10}K sec-1 and resolidification interface velocities of 1-20 m $\sec^{-1}$. A material of poor oxidation or corrosion resistance but low cost can be modified with a surface alloy which can show improved resistance. Likewise can wear and abrasion resistance be improved. Laser grain refining eliminates or minimizes surface defects such as inclusions, intermetallic compounds and pores, and improves the grain structure. Laser rapid-heat, shock hardening or slow-heat annealing-hardening can improve the surface mechanical properties, relieve stresses and tendency to stress corrosion cracking.

TABLE 6:3

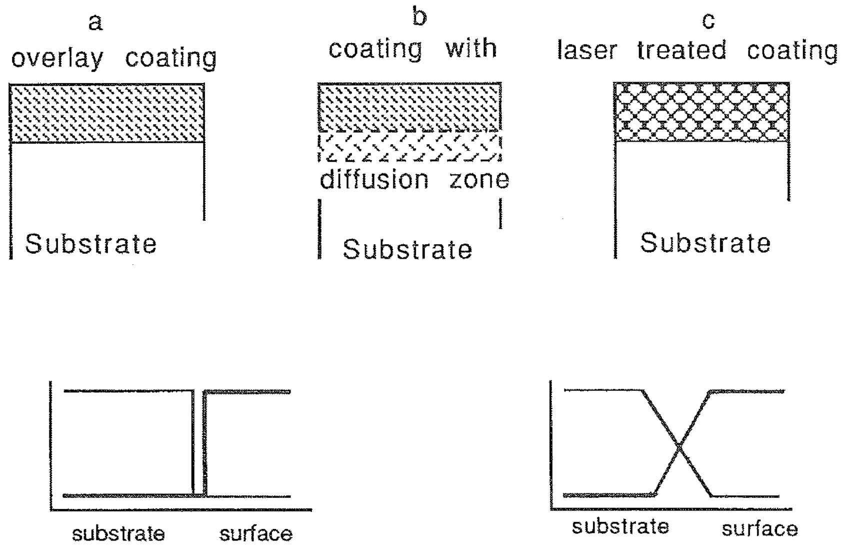
BEAM CHARACTERISTICS USED IN LASER SURFACE TREATMENT

Optical Telescope Parameter	State of Laser Beam	Beam Diameter/ Size; mm	Type of Laser Energy Profile	Application
f/7	Stationary	0.74	Gaussian	Alloying Cladding Glazing Grain refining
f/18	Stationary	1.9	Gaussian	Alloying Cladding Grain refining
f/125	Uni-directional oscillation	6.4 x 19	Rectangular Gaussian	Alloying Cladding Grain refining
f/125	Bi-directional oscillation	19 x 19	Square Gaussian	Alloying Cladding Annealing Transformation hardening
Beam Integrator	Stationary	15 x 15	Uniform square	Alloying Cladding Annealing Transformation hardening

The main limitation appears to be in the bulk area and size which can be conveniently handled by laser equipment. The advantage that a number of LST can be carried out in ambient atmosphere can be offset by the equipment and trained personnel cost. Its long-term advantages are, however, attractive.

6.2.3.1. LST Parameters:

Fig.6-3a,b show schematic diagrams of an overlay, a diffusion bond and LST surfaces and a typical concentration depth profile. In practice the substrate/coating interactions may not be as sharply divided and precise as in Fig.6-3a, but it shows adequately the effect on the interface. A simple overlay coating is hardly likely to exhibit any significant micro-structural change at the substrate/coating interface. LST is on the other extreme where a total surface modification can occur. Diffusion bonding, on the other hand, forms a diffusion zone of considerable thickness, with consumption of the original substrate and deposit materials. The advantage of LST on this is that the diffusion zone is very thin and very little substrate is lost in the dilution step. On the other hand, it can alter the total composition on the surface in a fraction of the time taken by diffusion bonding even to set up the interfacial zone. LST thus can 'create' or 'freeze' phases not captured to stability by any other means, because of the extremely rapid heating and cooling rates possible by laser heating.



Coating & Substrate concentration variation around the interface region

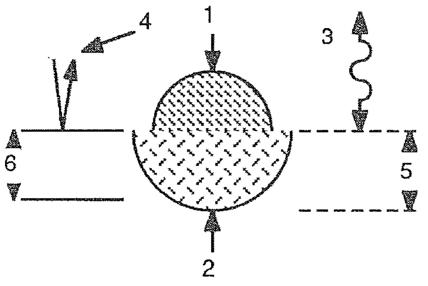
Fig.6-3. a,b: Schematic diagram of coating deposits & the effects of heat treatment & laser surface treatment

Fig.6-4 gives a schematic representation of the heat, absorption and reflection aspects of LST (Draper 1981). The temperature rise within the thermal diffusion layer is given by

$$T = \frac{(1-R)It}{C\rho(2Dt)^{1/2}}$$

where, R = reflectance of the surface, I = incident laser intensity, t = dwell time or pulse time of the laser output, D = K/C where K, C and ρ are respectively the thermal conductivity, specific heat and density respectively.

The incident laser intensity is absorbed by the metal within its electromagnetic skin depth, typically 10 - 100 nm and this is converted to heat. The heat rapidly diffuses away to depths directly related to the thermal diffusion length, i.e. $\sqrt{(2Dt)}$. The bulk of the solid then absorbs this heat. For T = 1000K at exposure times of 10 msec to 100 nsec quench rates can be 10^5-10^{10} $ksec^{-1}$. If metal loss is to be avoided, obviously the boiling point of the metal must not be exceeded.



1. optical spot size diameter
2. effective melt pool diameter
3. Intensity of the incident laser beam and the pulse or dwell time
4. the normal spectral reflectance of the surface
5. melt depth
6. resultant solid coating thickness when overlapped

Important laser beam parmeters are: Thermal Diffusivity D, melting point T and vapour pressure P of the coating A and the substrate B

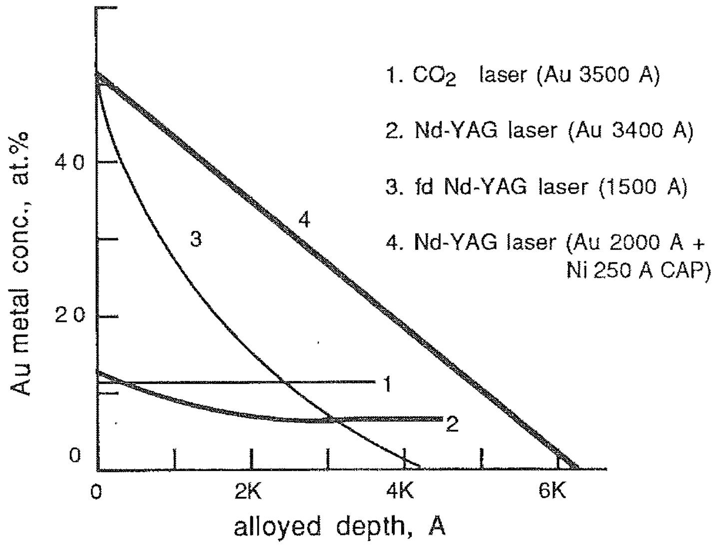
Fig.6-4: Laser beam parameters and the interaction of substrate - surface-beam configuration

Table 6:4 illustrates variation of alloy composition with speed and power of the laser beam (Draper 1981). Longer dwell times produce broader and deeper melt beads and more dilution in surface Cr-composition.

Much higher quench rates and regrowth velocities are possible with the 10-200 nsec laser pulses obtainable in Q-switched lasers. This would mean metastable surfaces even further removed from equilibrium than those produced by pulsed or relative motion continuous lasers are possible. The penetration depth is not more than 10000 AU. The technique would be particularly valuable in applying thin films of very expensive or strategic element surface alloy to a less expensive substrate. The problems in composition control are evaporation loss and "explosion" loss. Slower speeds (e.g. with CO_2 lasers) cut such losses but at the cost of greater alloying depths and hence need more material. A frequency doubled Nd-YAG laser appears to have offered a suitable compromise in alloying Au onto a Ni substrate giving a 50 atom% Au in a 1500 AU film (Fig 6-5) (Draper 1981).

TABLE 6:4

Velocity cm/sec	Melt Width, microns	Melt Depth, microns	Chromium %
38	326	99	11
50	259	51	23
63	276	37	31
75	167	20	58
88	202	42	35
100	133	14	80
125	133	18	60



Close agreement found between calculated and RBS-spectra estimated values. The long melt time in 1 has yielded a very uniform alloy composition by LST

Fig.6-5: Depth profiles of laser surface alloyed Au-Ni alloys.

The interplay between the laser parameters and material properties influence the emerging microstructure and metallurgical properties of the laser-alloyed or laser surface treated material. A detailed discussion is given by Mordike & Bergmann (1984). Non-transformable steels gain a more homogeneous and finer grain structure but show no significant change in hardness. Transformable steels can exhibit a variety of microstructures and a considerable change in hardness. Stringent control conditions are needed for laser treating Ti-alloys. Most high temperature alloys are suitable for LST.

6.2.3.2. LST Parameter Estimation:

The foregoing brief account on surface treatment links four laser operational parameters: (i) incident laser beam power (ii) laser beam diameter (iii) absorptivity and (iv) traverse speed. The depth of penetration is directly related to the power density which is a function of the beam power and diameter. With the diameter constant, the higher the power the greater the penetration; it could be almost a linear relationship (Draper 1981; Locke & Hella 1974).

Mazumder (1981) indicates that the photon drag detector is probably the most accurate of all modes by which the beam diameter is estimated. Gnanamthu (1979) estimated beam intensity from burn patterns on a slab of polymethylmethacrylate. A Gaussian beam diameter defined as the diameter where the power has dropped $1/e^2$ of the central value is recommended as it contains at that value more than 80% of the total power.

The most material-dependent laser parameter is absorptivity (or emissivity, reflectance). All heat transfer calculations for laser processing are based on the energy absorbed by the work piece. The reflectance requirement for laser suface treatment is almost nothing to that required for laser welding (LW). The faster, cleaner, reduced LAZ (laser affected zone) is obtained with the capacity of the workpiece to cut reflectance losses. But in both LST and LW the total laser efficiency is absorptivity-linked. Defined variously,

$$A = 112.2\sqrt{\rho_r}$$

where, A = Absorptivity and ρ_r = electrical resistivity, emissivity $\epsilon_\lambda T = 1-0.547/\sqrt{B} - 0.009\sqrt{B}$, where $-B = 0.667\rho_r(T)/\lambda$; $\rho_r(T)$ is the electrical resistivity (ohm-cm), T is temperature in deg. Kelvin for radiation wavelength λ (Bramson 1968).

Thus the estimated absorptivities are: when molten 2 and 3% for Al, Ag, Cu; <15% for Fe, Zr, 304 stainless steel and Ti-6Al-4V (at 300°C). This implies reflection losses are high. Reflectance losses can be reduced by applying an absorbant powder, or forming an anodized film (Arata & Miyamoto 1978), or by the use of a reactive gas; e.g. 10% O_2 in the shielding argon gas increased the welding depth almost 100% (Jorgensen 1980).

Metals are poor absorbers of infrared energy at room temperature, but above 10^6-10^7 W/cm^2 threshold, energy transfer can take place via a "keyhole", leading to much higher absorptivity. Multiple reflections within the keyhole can cut emissivity losses sufficiently to allow deep welding possible (Brown & Davis 1976). The threshold energy required by a laser beam to form such a keyhole is 1.5×10^5 W/cm^2, much higher than for an electron beam. This is why laser welding cannot handle thick materials unlike electron beam welding. However, laser welding of "difficult" materials is done with considerable success, e.g. Al- and Ti-alloys.

The laser traverse speed is a compromise between the melting and penetration the beam can achieve without causing damage and vaporization of the material being melted. Thicknesses greater than 3mm cannot be handled effectively for laser welding but is quite adequate for applying reasonably thick bulk coatings. The drawback arises from the attenuation of laser power caused by products formed _in situ_, e.g. plasma (Locke et al 1972a, 1972b). The traverse speed of the beam has to ensure total penetration and melting as the beam moves along. Electron beam welding scores over laser welding in its capacity to penetrate the work piece because the material absorptivity of the electron beam energy is not dependent on the keyhole reflections, its shape or extent.

Chande and Mazumder (1983) have illustrated a significant application of the statistical experimental design technique for composition control in LSA. A dimensionless parameter has been introduced (LASAP - Laser surface alloying parameter).

LASAP = $P/(pud^2)$, where P =incident power (W), p = shielding gas pressure at the surface, u = traverse speed (m/s) and d = beam diameter (m).

Another dimensionless parameter LAPP, (Laser-physical properties) is given.

LAPP = $Pd/(\rho\alpha u^2 d^2)$ where P, d and u are as defined above; and ρ & α are density and thermal diffusivity of the substrate; $(p/d^2)/\alpha$ = measure of the heat flux (the substrate's ability to dissipate this flux); $1/\rho u$ = measure of the mass flux in the melt pool, d/u = measure of time interaction and P/ud^2 = measure of the energy density.

LAPP quantifies the complex transport processes in LSA with respect to interaction time.

Processing conditions which lead to high alloy specie concentrations are accompanied by high cooling rates producing refined microstructures. Relatively wide beams (>1 mm dia) and long interaction times can produce zones of smooth flat surface profile (Christodolou et al 1983). When using alloying component elements or compounds which have high vapour pressure, surface losses have to be taken into acccount.

6.2.3.3. Features of LST:

Some of the noticeable features in LSA and LST are:

(i) The small beam width: the actual area that can be treated is so small that several passes by the beam are needed to cover an entire area.

(ii) Also, the laser beam melts only a fraction of the longitudinal traverse area which results in ripple-like solidification patterns.

(iii) The melting effects in (i) and (ii) result in a striated, banded, wavy appearance on the finished substrate.

(iv) The two hazards in LSM are porosity and microcracking. The rapid heating and cooling traps bubbles induced by convection in the melt pool, and thermal shock can generate microcracks.

Optimization of laser parameters for LST has been a study-exercise to most workers using the laser (Chande & Mazumder 1981; Mehrabian et al 1979). Correlation of laser processing parameters (power density and interaction time) with the properties of the resultant surface has been investigated from the conventional to the statistical type of analyses. Metallurgical analyses include structure, composition and other properties. These range over conventional optical, transmission electron and scanning electron microscopy; x – ray diffraction; spectroscopy; EDAX and ESCA; hardness; corrosion/oxidation; wear; high temperature stability and heat treatment tests and so on.

6.2.4. LASER ASSISTED COATING TECHNOLOGY

6.2.4.1. Surface Treating in General:

A comprehensive cross section of LST literature up to 1980 is available (Draper 1981) and has been updated (Draper & Mazzoldi 1986). LSA- components are applied to the substrates as powder, paste (slurry), paints, or as sputtered, sprayed or electrodeposited layers.

Laser equipment in conjunction with other coating procedures has been variously tested. Laser cladding, laser spraying, laser-assisted CVD (LACVD), Laser assisted PVD (LAPVD), and laser modifying of plasma coatings have been reported. There are definite advantages in these processes and their economic feasibility has to be established.

1. Extensive laboratory studies exist on ferrous alloys, in modifying the surface characteristics, composition and morphology. For instance, application of a stainless steel composition, or altering the structure completely or partially to obtain austenite, austenite-martensite etc. (Christodolou 1983). Similar studies have also been done on Ti-alloys (Bayles et al 1981; Peng et al 1981; Moore et al 1979) and laser glazing on Zr-alloy stabilized a martensitic structure (Snow & Breinan 1979).

Carbon can be laser surface alloyed into pure iron and 1% C + 1.4% Cr steel (Walker et al 1984; Steen & co-workers). The substrate was precoated with DAG graphite and then up to 12 successive laser surface meltings were given, re-applying the graphite coatings between each treatment. Up to 6% C was alloyed in. Case layers of about 0.2 mm with a bainite structure has been recorded on 6 mm thick Armco Fe. A 15 kW CO_2 laser was used to carburize a graphite dag coated substrate. A maximum temperature of 1051-1058°C was reached over interaction times 1 and 20 secs (Canova & Ramous 1986).

2. Ni-10Cr and Ni-15Cr alloys were laser treated to melt depths of 170-175 microns at a power density of $1.7x10^9$ W/m^2, with a speed traverse of 15-70 mm/sec. LST-treated healing Cr_2O_3 were found more resistant to cracking (Stott et al 1987). A general feasibility study on use of LST for fabrication of coatings resistant to high temperature degradation is given (Galerie et al 1987). SiO_2 coatings have been laser-fused onto Incoloy 800H samples (Ansari et al 1987).

3. Stellite coatings applied by TIG and oxy-acetylene torch were laser treated using high power Nd-YAG and CO_2 lasers. A CO_2 laser was also used to carry out laser coating. Laser modified stellite coatings were structure refined through to thin layers but their properties were not significantly improved. The oxyacetylene deposited coating, in fact, showed extensive crack formation on LST. The best results were obtained with the laser-applied stellite coatings (Tiziani et al 1987).

4. Dense crystalline ZrO_2 films have been deposited by pulsed laser evaporation (Sankur et al 1987). Deposition of conductors from solution with laser is reported (Auerbach 1985). Laser trimming of sputtered CrSi films covered with SiO_2 resulted in transforming the underlying CrSi with the top silica layer unaffected. Cr in CrSi is released on laser trimming to diffuse along leaving Si to oxidise (Masters 1985).

6.2.4.2. Laser Cladding:

Laser beams are particularly suited to apply cladding alloys with high melting points on low melting substrates. Wear, impact, erosion, and abrasion resistance, and high temperature corrosion resistance are the regime in which Co- , Fe- or Ni-base alloys are extensively used. Cast rods and pre-alloyed powders have been used for hardfacing. Self fluxing alloy powders, e.g. Ni-Cr-, Ni-base or Co-base alloy powder containing Si and B are flame sprayed and subsequently laser-treated. Oscillating and stationary laser beams have produced satisfactory, uniform, pore-free claddings.

Cladding materials range from alloy to ceramic, viz, Tribaloy, Ni-base, WC+Fe, TiC, Si and Al_2O_3. Shielding gases used are He, H_2, Ar, or oxygen as required (Gnanamuthu 1979). Vibro-laser cladding is an interesting variation in this section. Powell and Steen (1981) report that ultrasonic vibration (20 microns at 25kHz) during cladding reduced thermal stress-cracking and also porosity. The effects were monitored in situ by means of acoustic emission and later by optical macro- and microscopy, hardness and SEM studies.

A pulsed CO_2-TEA laser will melt the surface of coatings and thus seal porosity. A pulse length of 20 to 40 microseconds keeps the surface temperature below boiling. This is a useful treatment of plasma sprayed coatings which have a large fraction of open and closed porosity (lowers strength and corrosion resistance). A quick scan by a CW CO_2 laser is unsatisfactory for air-sprayed coatings as the expansion of gas-filled pores generates a spongy structure. A pulsed laser melts only the upper surface part of the coating. A plasma sprayed Ni coating was pulse laser treated with peak power pulses of 60 GJ/sm^2 and the open porosity decreased from 21% to 16% (Dallaire & Cielo 1982).

Detailed studies of laser cladding steel with stainless steel have been reported (Weerasinghe & Steen 1987). Tables 6:5 and 6:6 give a few representative data on laser cladding of various refractory and wear resistant materials and LST of steel.

TABLE 6:5

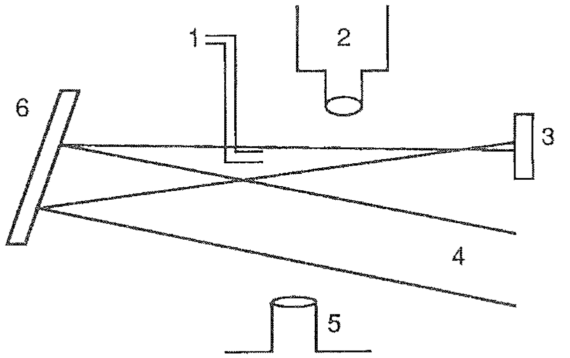
EXPERIMENTAL CONDITIONS AND RESULTS FOR LASER ALLOYING AISI 1018 STEEL

Alloying Elements	Cr	Cr, C	Cr, C, Mn	Cr, C, Mn, Al
Powder Coating Composition (wt%)	100 Cr	85 Cr-15 C	25 Cr-50 C -25 Mn	24 Cr-48 C -24 Mn-4 Al
Processing Conditions				
Laser Beam Size (mm x mm)	18 x 18	6.4 x 19	6.4 x 19	6.4 x 19
Oscillating/ Stationary Beam	Stationary	Oscillating (690 Hz)	Oscillating (690 Hz)	Oscillating (690 Hz)
Laser Power (W)	12500	5800	3400	500
Speed (mm/s)	1.69	21.17	8.47	8.47
Shielding Gas	Helium	Helium and Argon	None	None
Application Method	Slurry	Slurry	Spray	Spray
Depth (mm)	0.5	0.75	0.025	0.125
Width (mm)	6	25	25	25
Alloyed Casing				
Depth (mm)	1.95	0.38	0.13	0.66
Width (mm)	21	15	15	15
Composition (wt%)	16.0 Cr, 0.7 Mn	43.0 Cr, 4.4 C, 0.5 Mn	3.5 Cr, 1.9 C, 1.3 Mn	0.9 Cr, 1.4 C, 1.0 Mn, 0.5 Al
Hardness (R_C)	53	64	64	56
Major Microstructural Constituents	Martensite	Carbide M_7C_3	Martensite and Cementite	Martensite and Austenite

TABLE 6:6

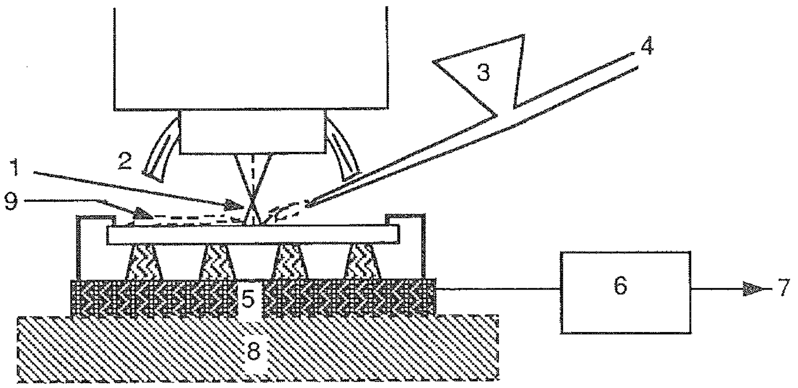
EXPERIMENTAL CONDITIONS USED FOR LASER CLADDING

Cladding Material	Tribaloy T-800 Alloy	Haynes Stellite Alloy No.1	Silicon	Tungsten Carbide and Iron	Alumina
Base Material	ASTM A387	AISI 4815	AA 390 Aluminium Alloy	AISI 1018	2219 Aluminium Alloy
Form of Cladding Material	Powder (Plasma Spray Grade)	Cast Rod (3 mm diameter)	Powder (44 μm size)	WC Granules (0.5 mm size) and Iron Powder (44 μm size)	Powder (0.3 μm)
Pre-heat Temperature, °C	20	250	20	20	20
Powder Application Method	Slurry	-	Slurry	Loose Powder	Loose Powder
Powder Depth (mm)	6	-	1	1	0.75
Powder Width (mm)	25	-	5	19	25
Oscillating/ Stationary Beam	Stationary	Stationary	Stationary	Stationary	Oscillating (690 Hz)
Laser Power (W)	12,500	3,500	4.300	12,500	12,500
Laser Beam Size (mm x mm)	14 x 14	6.4 (diameter)	5 (diameter)	12 x 12	6.4 x 19
Shielding Gas	Helium	Hydrogen and Argon	Helium and Argon	Helium	Oxygen
Processing Speed (mm/s)	1.27	4.23	8.47	5.50	8.47



1. powder feed 2. Pyrometry system 3. graphite
4. laser beam 5. velocity system 6. mirror

Fig.6-6: Schematic set up for monitoring powder propulsion



1. de-focused laser beam 2. water-cooled, reflector copper dome 3. powder-feed hopper 4. Argon propellant gas 5. 25 kHz ultrasonic vibrators set in rubber and housed in a steel box 6. ultrasonic amplifier 7. to A.C. supply 8. hydraulic controlled X-Y table; X-direction - melt bead running line; Y-direction - shift for overlapping laser tracks

Fig.6-7: Vibro-laser cladding - schematic diagram

(Steen & Powell 1981)

6.2.4.3. Laser Spraying:

Laser cladding and laser spraying are very related operations. A substrate may be clad by spraying when the material to be coated is in a powder/particle form. Cladding can also be done using sheet metal, and this can be later laser modified. Laser alloying is another term used in this context.

Fig.6-6 and 6-7 illustrate schematic arrangements for laser spraying and powder cladding respectively (Powell & Steen 1981). The coating powder is blown from a side, at an angle into a high power laser beam which heats the particles to their melting point and the molten droplets are then dispersed on to the substrate. Use of a highly polished, water-cooled copper dome above the work piece optimises the laser heating and reflection loss aspects to a better degree: (Powell & Steen 1981; Weerasinghe & Steen 1986; 1987). The process is not yet through to production levels (Steffens 1983), the disadvantages being the requirement of high laser power and reactions of the powder constituents in the ambient atmosphere. The latter aspect can be compensated for by maintaining a hovering envelope of a non-reactive gas. The cost effectiveness will be oriented to the choice of nitrogen, argon, helium or any other inert gases, together with the energy, equipment, and the strategic importance of the workpiece.

During boriding austenitic steels it was found that if the temperature at the point of impact of the laser beam rises above the substrate melting point, the resultant surface will be a mixed fusion composition. On boriding, the upper ferritic boride layer registered a hardness of 1400 HV sustained to a depth of 0.1 mm, decreased to about 850 HV over 0.1- 0.2 - 0.3 then fell sharply to 450 at 0.4 mm and 200 at 0.5 mm from the surface. (Sepold & Rothe 1979). Laser spraying of Ti and Cr has been reported (Yoneda et al 1988).

Hard metal matrix-ceramic composite layers for wear resistance have been laser-sprayed using a 10 kW, CW CO_2 laser beam oscillating with a frequency of 110Hz. 8-12 mm wide melt pools were formed on the IN 625 alloy samples. WC particles 45-75 microns were fed at rates of 0.35-0.5 cm^3/sec using helium at 35-85 kPa. Higher powder feed rates and lower gas pressures were necessary to inject the lighter TiC particles of 75-150 micron size. Relatively slow substrate velocities at 0.5-0.75 cm/sec were adopted to achieve 1-2 mm thick clad layer (Cooper 1986).

6.2.4.4. Laser Compaction & Laser Crystal Growing:

Coatings applied by thermal spray, plasma spray or vapour deposition can be laser-compacted to reduce porosity. The coating gets remelted either within the top thin layers or with a thin layer of the substrate depending on the LST parameters chosen. Optimum conditions were investigated on plasma sprayed IN 625 on type 316 stainless steel (Vasantasree & Hocking 1987). This results in an improved bonding, and reduced porosity, and the coating also solidifies in a finer crystalline form (Sepold & Rothe 1979). A laser pulse length of 20-40 microseconds was found to fill up the pores without overheating the material above its boiling point. A pulsed CO_2 TEA laser was used on plasma sprayed Ni (Dallaire & Cielo 1982).

Amorphous and crystalline materials can be produced from laser interactions with a suitable gas medium. Diamond from methane is one such novel product (Fedoseev 1981). Hydrocarbon droplets can be laser decomposed to yield spherical amorphous, or irregular crystalline graphite or diamond, or metastable forms of carbon. An infrared laser was used to a power density of 5000 W/cm^2. Particles up to 0.1 microns have been produced. LST needs sophisticated handling and cost-justified outlay, but has a vast scope in coating technology.

6.3. RAPID SOLIDIFICATION PROCESSING (RSP)

Rapid solidification is a particular form of consolidation of a coated surface. Materials used for coatings are either rapidly solidified even as they contact the substrate in droplet form or as vapour, or, a solid coated surface is remelted and rapidly solidified. Many coating processes discussed in chapters 3-6 are suited to achieve RSP in addition to their individual capabilities for producing specific types and ranges of coatings. A separate identity is given to RSP in this chapter in view of the fact that it is comparatively new as a coating process. Current RSP investigations are both in materials and coatings development (Wadsworth et al 1988; Das & Davis 1987; Kear & Giessen 1984).

Section 2.5 in Chapter 1 has already introduced amorphous coatings which are produced by RSP methods. Controlled metallurgical properties on bulk materials by surface modification are manipulated using RSP principles. Amongst PVD methods, electron beam evaporation, sputtering and plasma enhanced PVD are capable of producing 'glassy' deposits. Plasma assisted CVD produces amorphous coatings. These two categories produce non-structural deposits from the vapour phase. Laser glazing and electron beam glazing are surface modification methods which almost eradicate surface microstructural features to produce frozen vitreous states which are normally metastable phases when mass solidified from bulk melts.

Rapidly solidified coating is achieved by creating a very large temperature gradient between the substrate and the contacting film or by rapidly cooling the molten droplet of the coating material originally in a powder form. Rapidly solidified material in powder or ribbon form is produced by rapid quenching by melt spinning on cooled copper wheels, or by rapid quenching of atomized liquid or by splat cooling (Johnson 1986). RSP powder is used in spraying techniques as coating material and it has also been consolidated to required forms by hot isostatic pressing (HIP) or hot isostatic compression (HIC) methods. The ultimate advantage in RSP is achieved via microstructure control and it is recognised by the absence of microstructure or by being amorphous.

Amorphous phases of a normally crystalline alloy have been produced by irradiation (Mori et al 1984; Brimhall et al 1983; Cahn & Johnson 1986). Hydrogen dissolution in an alloy has caused amorphization (Yeh et al 1983). The amorphous phase generates at the grain boundaries and grows into grain interiors as the concentration of dissolved hydrogen increases (Yeh & Johnson 1986). Solid state amorphization has been reported from seveal laboratories; elemental mixtures of metal powders when mechanically alloyed in a high energy ball mill result in alloys with microstructures typical of RSP products (Yermakov et al 1981;Schwarz & Johnson 1983; Koch et al 1983; Schwarz et al 1985; Politis & Johnson 1986). Amorphous mechanical alloys in bulk form as filamentary and lamellar composites have also been reported (Atzmon et al 1984; Schultz 1985). Slow ball milling has been shown to transform even an initially homogeneous intermetallic compound to the glassy state (Schwarz et al 1985).

6.3.1. RSP MATERIALS

1. The best known, simple amorphous coatings are Ni-P (also Ni-B) coatings produced by electroless methods. These have also been produced by CVD in an rf plasma on nickel substrates using meta carbonyls $Ni(CO)_4$ and $Fe(CO)_5$ and metalloid hydrides PH_3 and B_2H_6 (Bourcier et al 1986).

2. Foil source of a predominantly amorphous Ni-Cr-Fe-Si-B alloy $Ni_{63.5}Cr_{12.3}Fe_{3.5}Si_{7.9}B_{12.8}$ and a slab source cast of crystalline $Ni_{55.3}Cr_{16.9}Si_{7.2}B_{21.6}$ were used in a dual-beam ion sputtering system for producing amorphous alloys. The foil source produced amorphous coatings under all experimental conditions. Deposition rates were slower from the slab source and also the coatings were partially polycrystalline and amorphous (Panitz 1986).

3. Electron beam surface melting of Ni-Cr-Mo-V steel with traverse speeds 4.4 - 36.4 cm/sec resulted in grain refinement and increased hardness. The steel was austenitized at 980°C for 1 hour, oil quenched, tempered at 620° for 6 hours and oil quenched, held for 4 hours at 400°C for stress relief and then treated by electron beam melting and cladding. Cladding was done by pressing a uniform layer of 100 mesh size $Fe_{80}P_{13}C_7$ alloy powder, and electron beam melting it at 50-200 W beam power (for varying powder thicknesses) at similar traverse speeds. Hardness values were in the range of 880-1150 VPN for these amorphous alloy claddings (Mawella & Honeycombe 1984).

4. Electron beam glazing of high speed steel using a 1 - 15 KHz oscillating beam at 1 - 100 cm/sec has resulted in a 3-35 mm wide RSP. Homogenization of the substrate as a pre-treatment step was definitely advantageous to the subsequent beam glazing (Strutt et al 1984). Microstructure 'tailoring' by electron beam glazing has been achieved on hardfacing alloys, viz. Stellite 6 with and without TiC, TiB_2 particle strengthening (Kurup et al 1984).

5. Sputtered Si_3N_4-SiO_2 multi-layer amorphous sandwiched coatings show excellent resistance to laser damage when used as optical filters. Dendritic silicon nitride alternates with amorphous silica coating by selectively introducing N_2+Ar and O_2+Ar during the sputtering process. Control of the reactive gases allows the interface betwen layes to be chemically graded (Guenther 1986; Courtright 1987).

6. Co-sputtered 304 stainless steel and W on 304 stainless steel substrate resulted in an amorphous structure which conferred a superior resistance to stress corrosion cracking and pitting (Wang & Merz 1984). Refractory metals such as W, Ta etc. when co-sputtered or plasma sprayed along with stainless steel were found to stabilize the amorphous structure up to 400-600^oC.

7. Thermal barrier coatings have been known to have columnar microstructure excellent for thermal shock resistance but poor for condensate corrosion. Plasma spraying and PVD microstructures provide additional defence by applying dense closeout top layers, or better as multiple sealing layers. On an IN 792 substrate a CoCrAlY bond coat was covered with a columnar sputtered ZrO_2-$20Y_2O_3$ initial layer. This provided a strain tolerant coating at the interface. A negative bias was applied to disrupt the columnar growth pattern, once the desired thickness was reached. This interrupted the columnar crystal growth and deposited a dense intermediate amorphous sealing layer. The process was repeated to result in three columnar segments with three sealing layers. The life time of the base coat was increased by a factor of three, the thermal shock resistance was high (survived five water quenches from 1000^oC) and improved corrosion resistance to molten sodium sulphate (Prater 1987).

8. Laser glazing to obtain glassy alloys has been studied for Ti-Au, Ti-Co, Ti-Cr and Ti-Zr systems. All except Zr-Ti resulted in amorphous surface alloys (Von Allmen & Affolter 1984). Ultra-fast cooling at the rate of 10^{12} deg./sec by pulsed laser quenching has been investigated (Lin & Spaepen 1984). Laser glazing for wear and corrosion resistance has been done on Ni-base superalloys (Yunlong et al 1984) as well as to obtain amorphous $Fe_{82}B_{12}C_6$ and $Fe_{82}C_{18}$ alloys.

9. Superalloy ribbons show a gradual progression from a dendritic to cellular and planar solidification in a melt spinning process (Huang & Laforce 1984).

10. Hardfacing alloys with excellent resistance to wear, oxidation and corrosion have been produced by rapidly cooled inert gas atomized powders and plasma spraying. The 'Toh-boride' system was investigated. Quaternary alloys of five compositions were prepared in the series Ni-Cr-Nb-B and Ni-Cr-Ta-B (Lugscheider et al 1987)

6.4. DROPLET TRANSFER COATINGS BY SPRAYING

Metal spraying coating was invented in 1909 (Kasperowicz & Schoop 1920). Table 6:7 is a summary of spraying processes developed since then. Fig.6-8 gives an idea of processes available and areas are identified for process variants still to be explored (Kretzschmar 1973). A major advantage of spray coating is in the production of graded coatings by gradual change in the feedstock. Different materials can be sprayed simultaneously and any coating composition is possible, although microhomogeneity may not be achieved (depending on solubilities).

Five spraying techniques are given in the next five sections: 6.5 to 6.9.:- Liquid metal-, Wire explosion-, Flame-, Detonation Gun- and, Plasma-spraying. Plasma spraying was carried out first at atmospheric pressures and later developed into the low pressure plasma spraying and vacuum plasma spraying methods. New advances such as the shrouded plasma spraying technique which offers the plasma coating route on a more economical basis for large-sized substrates and underwater plasma spraying are also reported. Plasma as a medium has been harnessed in many coating techniques. Plasma-assisted vapour techniques are PAPVD, PEPVD, PACVD and PECVD methods. On that basis section 6.5. may be considered to deal with plasma assisted molten media deposition.

TABLE 6:7

A SURVEY OF METAL SPRAYING PROCESSES

Type of Energy	Source of Energy	Atomising Gas	Material Form	Environment	Process	Practice Status
Electrical resistance heating	Induction heating	Argon	Molten metal in a crucible	4, (2)	Osprey (Molten metal spraying)	Effective
	Induction heating	3	Wire (a)	1	In-chamber induction spraying	Little used
		2	Wire	2		
	High Voltage	None	Wire	1 2	High Voltage Flame Plating (capacitor discharge)	Being developed
Electricity	Electric arc	3	Two Wires	1	Electric arc spraying	Widely used
		2	Two Wires	2	In-chamber arc spraying	Being developed
	Plasma	None	Powder	1	Plasma powder spraying	Widely used
				2	Plasma powder in a chamber	Being developed
Chemical reaction	Fuel gas flame/3	None	Powder	1	Powder flame spraying	Little used
	Oxy-fuel gas flame	None	Powder	1	----------- " ---------	Not much used
		5	Powder	1	---------- " --------	Widely used
		-- " --	Wire	1	Oxyacetylene wire spraying	Very widely used
	Very rapid combustion	None	Powder	1	Flame plating	Being developed
		2	Powder	1, (2)	---- " -----	Not much used

Note:- 1. Normal atmosphere; 2. Shielding gas; 3. Compressed air; 4. Vacuum; 5. Compressed gas; numbers in parantheses indicate an alternate route. a: Wire can be single or multiple, or powder-cored; powder and wire can be 'fed' simultaneously.

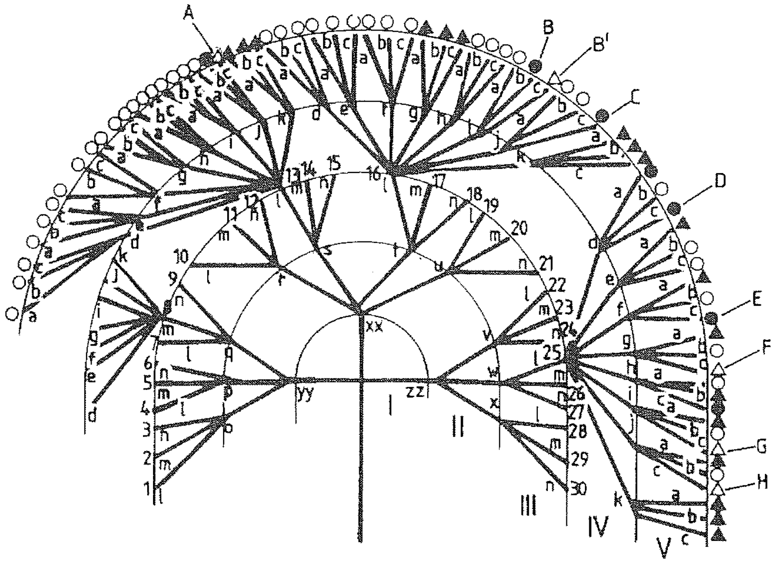


Fig.6-8
Energy Combinations & Process Variables Available & Explored for High Temperature Spray Treatment of Substrates

Segment No.	Process Variable	Segment No.	Process Variable	Segment No.	Process Variable
I	Type of Energy	II	Kind of Energy	III	Working Gas
IV	Type of Filler Material			V	Atmosphere

Section	Process Variable	Section	Process Variable	Section	Process Variable
I xx	Electricity	I yy	Beams & Waves	I zz	Chemical Reaction
II o	Ion Beam	II p	Laser Beam	II q	Electron Beam
II r	High Voltage Heating	II s	Induction Heating	II t	Arc
II u	Plasma	II v	Explosion-Combustion	II w	Oxy-fuel Flame
II x	Compressed Air-Fuel Gas Flame				
III l	Compressed Air	III m	Shielding Gas	III n	Without Air
IV d	Rod	IV e	Strip	IV f	Wire & Powder
IV g	Powder	IV h	Cored Wire	IV i	Two or More Wires
IV j	One Wire	IV k	Liquid		
V a	Vacuum	V b	Inert	V c	Air

Peripheral Notation (Clockwise)

A: High Frequency Spraying With One Wire
B: Arc Spraying in Shield Gas Chamber
B': Arc Spraying
C: Arc Spraying With One Wire
D: Flame Spraying With Ceramic Rods
E: Flame Spraying With Wire & Enclosure
F: Flame Spraying With Powder
G: Flame Spraying With Two Wires
H: Flame Spraying With One Wire

○ Possible Variant   △ Usual Variant   ● Tested Variant   ▲ Improbable Variant

Comments:- Clearly, the left hand segment was not much explored, viz. beams and waves (electron, ion, laser)/part electrical, in all media (air, gas, inert, vacuum) with filler materials and various working conditions. Beams and waves, on their own, are incapable of creating the coating material in a form viable enough to realise the end product as a **heavy duty** coherent deposit. PAPVD & PACVD developed as later techniques have enabled tribological deposits and many variations in multi-layer deposits.

6.5. COATING BY PLASMA SPRAYING

6.5.1. FUNDAMENTAL ASPECTS:

Plasma spraying technique has been practised for more than 25 years, but its fundamental technology is poorly established. Plasma generation, jet formation, particle injection, particle heat and momentum transfer, particle impact onto the substrate - its state and form, and, the post deposition substrate/deposit condition are the several aspects which have to be defined and understood (Pfender 1988).

Basically, the powdered coating material is carried in an inert gas stream into an atmospheric pressure or a low pressure plasma. Any coating thickness is feasible. Plasma generating equipment is available over a wide range from microplasma (1-10A) to mechanised plasma (100-400A) and the process (BS 4761, 1971) is well documented (Malik 1973; Houben & Zaat 1973; Anon. 1975; Tucker 1978; Anon. 1983; Kvernes 1983; Bennett et al 1984).

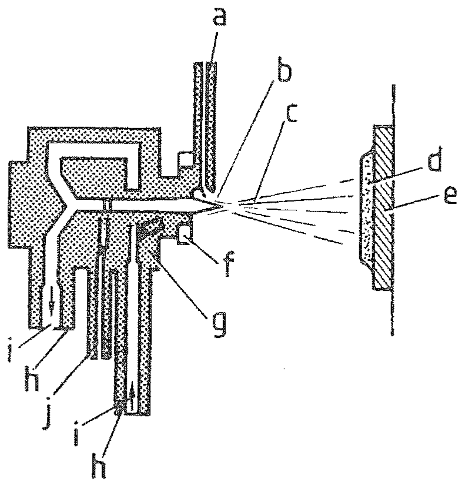
Frequent problems with plasma sprayed coatings are porosity and poor adhesion. The adhesion of plasma sprayed ceramics to metals is generally poor but can be considerably improved if a sprayed bond-coat or interlayer is used (e.g. Ni-Al, Mo). Special care is needed, as in electroplating, to clean and prepare the surface to be coated. Rough lathe turning is suitable for heavy coatings on large components (Steffens 1983) but unsuitable for aircraft components under stress. Grit blasting is also used for surface preparation and is claimed to provide the means for a strong mechanical bond (Wigren 1988).

The effect of quantified surface preparation parameters on adhesion of Al and Zn plasma coatings on steel has been studied. An electrochemical method for measuring true surface area, including the smallest irregularities, is given. The bond strength of arc sprayed Al is 3 times that of flame sprayed Al and Zn and of arc sprayed Zn. Further work is needed on quantifying the substrate surface properties which can determine coating adhesion and other relevant properties of powder materials (type, grain shape and size distribution). For low rust steel there is a linear relation between cleanliness (=reflectivity) and adhesion. Adhesion increases with increasing surface roughness (defined in a specific way). Arc sprayed Al has uniquely good adhesion with inferior cleanliness and topography, but flame sprayed Al and Zn and arc sprayed Zn need much stricter preparation (Bardal 1973). Sputter cleaning before spraying is worth investigation for possible improved adhesion.

6.5.2. ATMOSPHERIC PRESSURE PLASMA SPRAYING

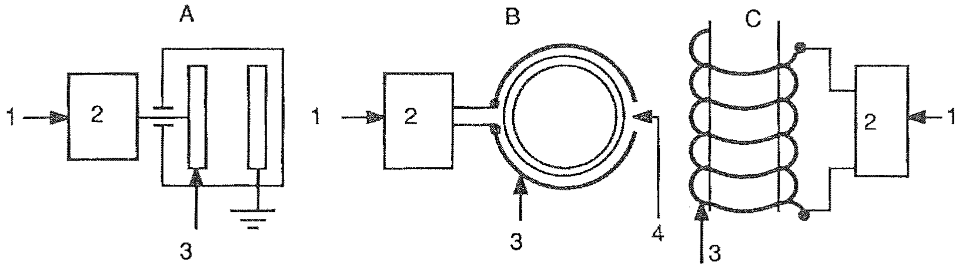
A plasma torch has a water cooled Cu anode and W cathode. Typically, Ar (or any other carrier gas) flows around the cathode and through the nozzle anode. A d.c. arc is held and the plasma (ions and atoms) emerges at $6000-12000^{o}$C to about 1cm from the nozzle. Further out the temperature falls rapidly to $<3000^{o}$C at 10cm, and still further out the temperature falls due to air entrainment (Nicoll 1984; Steffens 1983; Bennett 1983). Near the nozzle the gas velocity is 200 to 600 m/s while the particle velocity is only 20m/s. So the particle acceleration (due to frictional forces) is about 100000g. 18 micron particles reach 275m/s (maximum) at 6cm from the nozzle. Larger particles reach lower velocities, which gives them more melting time. Low density material particles reach higher speeds but also decelerate more. Fig.6-9 gives a schematic of a plasma spray gun head (Steffens 1983); Fig.6-10 shows a few electrode systems used for plasma discharge processes and Fig.6-11 gives an idea of plasma energies (Thornton 1980). Fig.6-12 shows a plasma coating torch with alternate powder injection locations.

The extremely high temperatures reached by the plasma can melt even very refractory powders into a molten mist (low mp materials, e.g plastics, can also be sprayed). The plasma jet is about 5cm long and nozzle to substrate distance is about 15cm. The carrier gas is Ar + H_2, or N_2 and H_2, flowing typically at 3.5 litres per minute (Dudco et al 1982). H_2 and N_2 raise the power level due to their high thermal capacity. Adding He allows an increased gas flow (up to 600m/s) and thus higher particle velocities, giving higher bond strength and coating density.



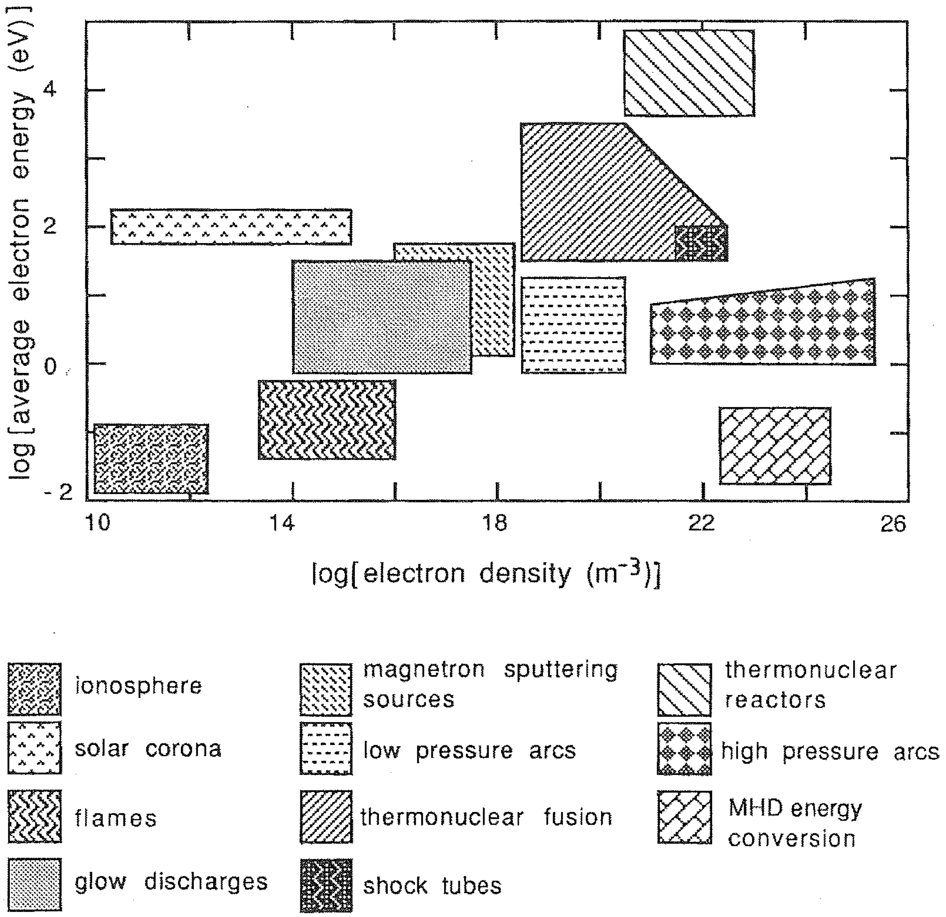
a. Mixture of powder & gas
b. Plasma flame
c. Spray cone
d. Coating
e. Substrate
f. Anode
g. Cathode
h. DC for electric arc
i. Cooling liquid
j. Gas

Fig. 6-9: Spraying Head - Cross Section of Plasma Spray Gun

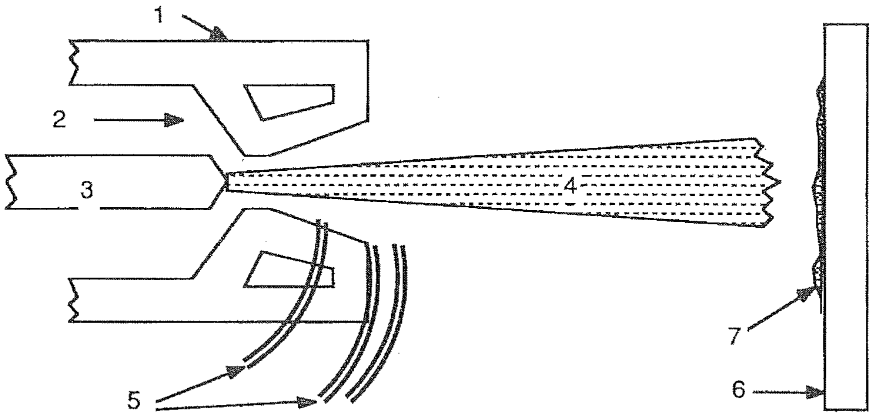


1. rf source 2. compatible network 3. electrode 4. dielectric walled tube
A. Planar electrode B. Clam shell electrode C. coil electrode

A selection of electrode systems used for plasma discharge in coating processes
FIG.6-10



Electron Density & Energy Regime of Plasma from Various Sources
Fig.6-11



1. water-cooled anode 2. gas stream 3. centre cathode 4. plasma stream carrying the injected powder via a carrier gas 5. powder injection location alternatives 6. substrate 7. coating

Fig.6-12: Schematic diagram of a plasma coating torch and substrate

Interacting parameters influencing plasma coating:-

a. Plasma torch: Relative movement of torch and the torch-substrate distance;

b: Plasma: Gas composition, the heat content, temperature, air dilution and velocity of the plasma stream

c. Powder: Particle shape, size distribution and the individual constituent composition within the particles; dwell time in the plasma stream

d. Substrate: Temperature - initial and during coating, residual stress effects, quenching rates of the incident coating material

But at high gas flow rates about 80KW is needed to melt the powder (typically about 700 amps). A water-stabilized plasma torch has been described (Vesely 1973) in which a water jet enters the plasma, liberating H_2.

A plasma is a very high energy state and thus transfers heat very fast to the powder, reducing the necessary dwell time at high temperature which minimises the oxidation of metal powders. Oxidation is also minimised by the inert nature of the heat source. An unlimited area can be coated. Marchwood Engineering Laboratories (CEGB, UK) have devised a plasma spraying shielding box which is attached to the torch and is contoured to half-fit on a tube being sprayed. The exit, at the tube, is double-walled, to prevent back-entry of air. Plasma spraying rarely heats the substrate > 320°C and it is usually < 150°C. Distortion of substrates is indicated in Table 6:8. It is evident that plasma spraying is the only process that does not introduce component distortion. A high frequency plasma (instead of d.c.) does not contaminate the coating with electrode materials and can be used with oxygen as the carrier gas in order to generate oxides at a high rate by injecting halide into the flame of an oxygen plasma (Gani & McPherson 1980).

TABLE 6:8

A SURVEY OF HARDFACING PROCESSES

Process	Deposit		Component	
	Thickness mm	dilution %	Heating	Distortion
Gas Metal Arc (GMA)	2.5	30	medium	high
Gas Tungsten Arc (GTA/TIG)	1.6-5	5-10	medium	medium
Open Arc	2.5	30	medium	high
Oxy-acetylene	1.6-5	5	high	high
Plasma Spraying	1.25	nil	very low	nil
Plasma Transfered Arc (PTA)	0.25-6.4	5	high but local	medium
Powder Welding	0.08-0.2	5	medium	medium
Shielded Metal Arc	>= 3.2	10-25	low	high
Spray Fusing	0.8-2.4	nil	high but uniform	low
Submerged Arc (SAW)	>=3.2	20-30	low	high

Note on high degree of component distortion: In large masses distortion may not be marked but cracking might occur, especially with harder grades.

Optimization of plasma spraying processes has been attempted in recent years to decrease coating porosity and achieve better adherence. The deposition efficiency is strongly influenced by both particle size and distribution (Brunet & Dallaire 1987). The various parameters identified for plasma torch, plasma, coating material, and workpiece are as follows (Wuest et al 1985):

Plasma torch: relative movement and workpiece standoff distance;

Plasma: Gas composition, heat content, plasma stream temperature, velocity, and air dilution of plasma stream;

Coating powder: particle shape and size distribution, elemental distribution within the particles and dwell time in plasma stream;

Workpiece: temperature, residual stress control and particle quenching rates.

A nozzle-electrode set that had already been in spraying operation for 38 hours appears to have given deposition efficiencies >50% with the best optimised working conditions.

A laser two-focus velocimeter has been used to monitor particle velocity accurately at 45 kPa (340 Torr) (Smith & Dykhuizen 1988). A smaller particle size reduced coating porosity (Pawlowski 1987) and automated powder mass flow monitoring and control system is reported (Saenz 1988). Power output of 80 kW in the Mach 2 velocity range produced very dense coatings not obtained by normal air plasma spraying (Lugscheider et al 1987). Molten powder jets emerging from a twin injector system of powder feed were found to cross without interference with each other to produce two separate deposition areas. Partially molten particles produced globular deposits while fully molten particle flattened on to the substrate on contact (Mazars & Manesse 1987). An analysis of velocity and energy of Al, Al_2O_3 and W powders in an Ar plasma jet is given and operating conditions recommended for good coatings (Perugini 1976). 30% of the plasma energy is used in accelerating and melting the W particles with 5% for the melting.

To produce dense strong deposits most of the particles must be molten before impingement and must have sufficient velocity to splat into the irregularities of the previous splats. Powder-plasma interactions are a prominent aspect (Nicoll 1984). Many coatings contain easily oxidized elements, e.g. Al, Mo, Ti, and then plasma spraying at low pressure (20 mbar) or in Ar becomes advantageous. Ti coatings are produced if $TiCl_4$ is passed into an Ar plasma jet (Ohno 1979). The substrate must be at a high temperature or a Ti subchloride is deposited. Rare metals like Re and Pt are plasma sprayed (Kirner 1973). Table 6:9 gives an idea of the oxygen content in a few plasma deposited metallic coatings (Tucker 1978). Powder size distribution is controlled , e.g. 5 to 45, or 45 to 70 microns. This depends on surface finish or thermal shock properties, e.g. ceramic thermal barriers: 20 to 90 micron. A high pressure jet can restrict entry of fine particles to the hot zone.

Table 6:9

OXYGEN CONTENT OF PLASMA DEPOSITED METALLIC COATINGS

Coating material	Cu	Mo	Ni	Ti	W
Oxygen content (%) Conventional coating	0.302	0.710	0.456	>2.0	0.274
Coaxial gas Shielded coating	0.092	0.160	0.151	0.730	0.030

Bonding of a coating is due to: mechanical bonding (contouring around the surface topography and interlocking with it) metallurgical bonding (interdiffusion) and physical bonding (van der Waals forces). Particle reaction with carrier gases has to be prevented, e.g. Y in a MCrAlY particle reacts with H_2 in $Ar+H_2$ plasmas. H_2 should be avoided in cases such as this.

Changes, in the plasma, affect the microstructure of coatings. W and Cr carbides, show these changes. WC in a Co binder has wear resistant properties. During normal sintering production, Co diffuses into the WC and is precipitated out again during cooling, thus forming a bonded structure. But during plasma spraying the WC fuses and the Co in it has no time to escape on cooling to form a bonding matrix. Further, $WC+W_2C$ particles in a Co coating decompose and oxidise, losing carbon due to their solution in molten Co. The carbon then evaporates as CO and CO_2. WC + Co compositions prepared via powder metallurgy route are unsuitable for plasma spraying. Further work in this area is desirable. Table 6:10 gives some data on plasma deposited WC.

Table 6:10

EFFECT OF POWDER SIZE ON THE STRUCTURE OF PLASMA DEPOSITED WC

Powder size microns	Apparent density g/ml	Bulk density g/ml	% theoretical density	Porosity	Apparent hardness Kn500
Coarse (10-105)	0.5	8.7	60	17.1	538
Medium (10-74)	13.0	11.1	77	14.5	684
Fine (10-44)	14.2	13.0	89	8.5	741

Plasma spraying of carbides often does not give a homogeneous coating whereas ceramics such as alumina do (Basinska-Pampuch & Gibas 1976). $WC+W_2C$ form in an air plasma medium rendering the deposit superior in hardness and finer microstructure to that produced by vacuum plasma spray. However, the latter shows a better wear resistance because the brittle W_2C is absent (Tu et al 1985; Vinayo et al 1985). Complete fusion is difficult while plasma spraying high melting point materials, e.g. TiC, but sometimes this may be an advantage from the microstructural point of view. Partially molten particles are embedded in a network of x10 smaller grains which are recrystallized from the molten impacted fraction. Plasma melted TiC also undergoes high decarburization in both air and argon atmospheres (Fournier et al 1985).

Fully stabilized (20% yttria) and partially stabilized (8% yttria) zirconia with Si impurity level at 0.2-4%, air plasma sprayed and sintered, acquired up to x3.5 its original strength and x4 its original modulus. The improvement is correlated to a change from the as fabricated state of mechanical interlocked network to a chemically bonded system (Eaton & Novak 1987). A plasma sprayed bond coat of Co 32Ni 21Cr 8Al 0.5Y along with 8 wt.% yttria stabilized zirconia top coat sprayed on Hastelloy substrate has been tested for hot corrosion (Tjong & Wu 1987). LST has been a key modifying procedure for plasma sprayed coatings. LST of alumina and zirconia stabilized separately by yttria and magnesia produced significant structural modifications (Iwamoto et al 1988).

A study of Cr_2O_3 plasma spraying showed best results are obtained with 15 KW power, 30 l/minute of N_2 + 5 l/minute of H_2, 800g/hour of powder flow, 30 to 50 micron powder size, projection distance 12 cm, sand blasted steel targets at right angles. Spraying parameter variations have been discussed for chromia spraying (Boch et al 1976). Plasma coating of ceramics onto steel vessels used for holding molten Zn for galvanizing prolongs life (Vasquez et al 1976). Typical plasma conditions are 650 amps arc current, 35 volts arc voltage, 50 Hz frequency, 900 g/h powder feed rate, substrate temperature 200°C, 10 to 15 cm spraying distance.

Materials like ZrN, MoS_2 and the fluorine resistant coating CaF_2 can be plasma sprayed (Kirner 1973). ZrN decomposes slightly and MoS_2 forms some Mo_2S_3. Masking and materials selection is discussed and 80Ni20Cr plasma coatings are described for sputtering target use (Downer & Smyth 1973).

Ceramic composites by plasma spraying are well known. Metal-ceramic composites, both substrate reinforced and free forms have been fabricated (Quentmeyer et al 1985). Stainless steel mandrels are grit blasted with alumina plasma sprayed with 0.05-0.08 mm NiCrAlY. ZrO_2-$8Y_2O_3$ is then plasma sprayed to about 0.38 mm thickness to form the composite. The metal is subsequently dissolved in a 5/1 HCl/HNO_3 acid to obtain the ceramic composite free form. Zirconia-yttria ceramics have also been plasma sprayed directly on SiC. Fibre-reinforced ceramic cores have also been tried as substrates but poor adhesion and surface distortion have retarded their development. Cu and Pt have been electroplated through into the pores of plasma sprayed ceramic coatings (Hendricks et al 1985).

Plasma spraying is used for composite fabrication, e.g. B fibres in an Al matrix. A layer of the matrix as Al foil, or Al plasma-sprayed onto a mandrel, is wrapped with a spaced array of reinforcing filament which is then enveloped by spraying on more Al while the mandrel is rotated. A multilayer array has voids but these can be removed by hot pressure; or stacked monolayers can be prepared free of voids (Kayser 1973). A boron fibre reinforced pressure vessel can be made this way, a thin walled shell or inner vessel being used as mandrel. A ceramic matrix is also feasible. Carbon fibres need electroplating before incorporation.

6.5.3. NEW DEVELOPMENTS IN PLASMA SPRAYING:

Two new advanced techniques may be mentioned here, viz. Shrouded plasma spraying (SPS) and Underwater plasma spraying (UPS).

Shrouded air plasma spraying is a recent development in producing diffusion and thermal barrier coatings and bonding layers. Work on MCrAlY, MgO ZrO_2 and ZrO_2-7 wt.% Y_2O_3 have shown that substantial advantages may be realized using shrouded inert gas plasma torches operating in open air as against vacuum and low pressure plasma spray methods. The stringent requirement is that the starting powder must have very low oxygen content, vacuum melted, and argon-atomized to the required composition and sized to the uniquely designed plasma torches. The coating process flow chart is cut down by 50% by using shrouded plasma method and plasma spraying becomes more economical while retaining a high quality output (Taylor et al 1985).

Underwater plasma spraying offers much scope for the deposition of wear and corrosion resistant coatings on submerged substrates. Underwater processing drastically reduces noise, radiation and dust while giving a substantial improvement in quality. UPS was first carried out at shallow depths 300-500 mm (Schafstall & Szelagowski 1983) but is currently under development for processing at greater depths to meet demands from stationary and mobile offshore structures (Lugscheider et al 1987). Powders made from self-fluxing Ni-based hardfacing alloys, Colmonoy 5, 52 and 42 with metalloids boron and silicon to reduce oxide films on base metal have been used (Knotek et al 1975). Other materials such as oxides, intermetallics, high alloy steels and corrosion resistant alloys are under scrutiny. The Ni-based alloys sprayed by UPS were free of cracks, with homogeneous microstructures of low porosity. The spraying distance was a critical parameter amongst all the parameters for plasma spraying. For UPS it is greatly reduced. The plasma has been ignited both above (Karpinis et al 1973) and below water (Lugscheider et al 1987). Coatings 100-300 microns have been deposited depending on the operating parameters.

6.5.4. LOW PRESSURE & VACUUM PLASMA SPRAYING

Some reactive materials cannot be sprayed in air. This problem is avoided by using low pressure plasma spraying (LPPS) which also increases particle velocity, giving pure and high quality coatings. The plasma jet is longer and so greater working distance is needed to avoid overheating. The LPPS jet velocity is up to mach 3, giving low porosity and good adhesion. The low particle dwell time requires powers up to 120KW to spray refractory materials.

The average coating rate is 25 microns per second over a circular 75 mm^2 area at 40cm distance, for most metal powders; for ceramics the rate is about half this. The density is typically 99% of the maximum possible. An advanced system description is given. Typical LPPS equipment are shown in Fig.6-13, 6-14 and 6-15 (Nicoll 1984; Steffens 1983; Muehlberger 1973).

The operating pressure is 50 to 70 mbar. The exhaust gas is filtered and cooled before reaching the vacuum pump. The inlet velocity distorts the arc about 50cm towards the substrate to be coated and additional power is needed to form the transferred arc which provides cleaning and rapid preheating of the substrate for coating, by transfering some of the arcing to the substrate. The powder is preheated and pressure fed to the nozzle. The large LPPS jet increases the heated surface area of substrate and small differences in spraying distance are acceptable. Higher powder losses and a lower energy density of the LPPS jet are sustained, compared with air plasma spraying. To avoid unwanted gas/metal reactions, powders and gases used are oxygen-free and the equipment is evacuated to 0.2 mbar before starting spraying. Successful LPPS coatings include the well-known Co(Ni)CrAlY used on gas turbine blades. Houben and Zaat (1973) give a mathematical analysis of LPPS torches.

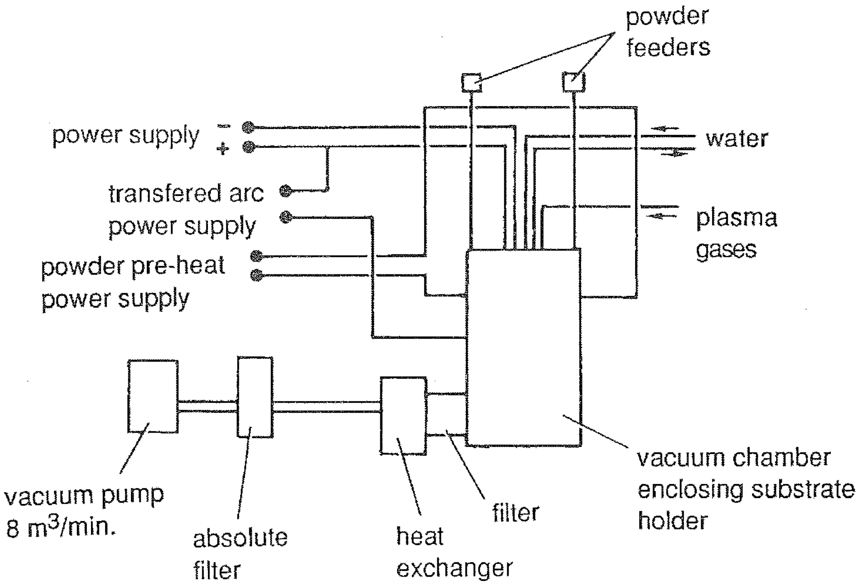
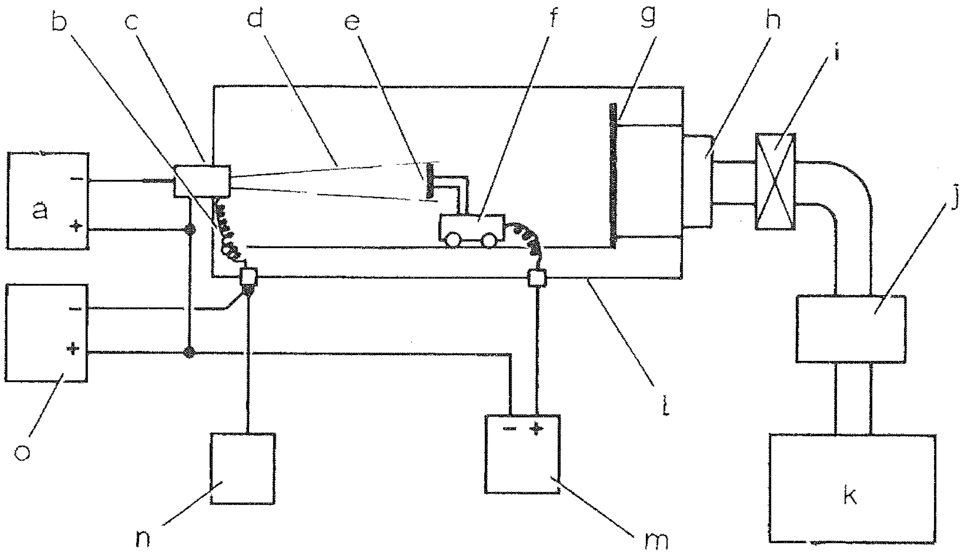
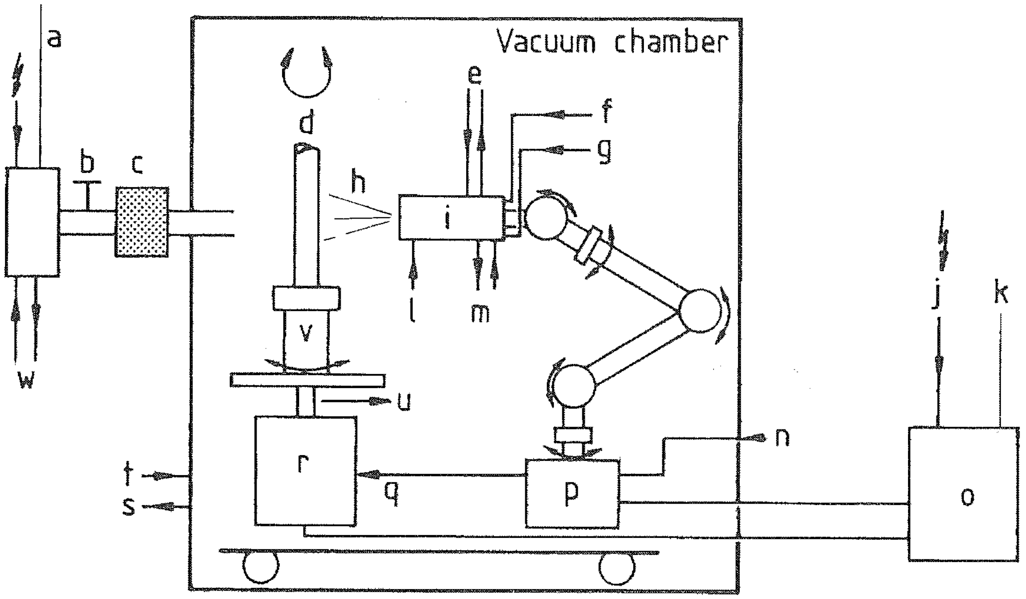


Fig.6-13: Low Pressure Plasma Spray Unit - Schematic



a. arc power supply; b.powder pre-heat tube; c. plasma generator; d. plasma powder stream; e. substrate to be coated; f. trolley; g. heat shield; h. filter; i. gate valve; j. roots blower; k. pump (mechanical); l. coating chamber; m. power supply (transfered arc; n. powder feeder; o. powder pre-heat power supply

Fig.6-14: High Energy Plasma Coating - Schematic Diagram



a. VPS control cable console; b. valve; c. dust filter; d. substrate to be coated; e. water-cooled power supply; f. gas inlet to plasma torch; g. plasma triggering unit; h. plasma jet; i. plasma torch; j. mains supply; k. plasma control cable; l. powder feed; m. torch connexion; n. argon cooling; o. robot control; p. robot; q. workpiece holder+argon supply; r. worktable (rotary); s/t. cooling water to spray chamber; u. power connexion channel; v. clamp

Fig.6-15: Vacuum Plasma Spray Unit - Schematic

In given plasma conditions there is likely to be an optimum powder particle size which will be melted and transported with enough momentum. Smaller particles may be vaporized and large particles may be incompletely melted giving a weak porous coating. The effect of powder size on adhesion of plasma sprayed coatings is discussed. Flow properties and feed systems are also described. Coatings 3 microns thick are obtained from metal powders 1 to 5 microns diameter. Finer powders do not necessarily give a surface smoother than 1 micron (result for Ni coating). Ultrafine particles tend to agglomerate in flight, giving lumpy coatings. No difference was found in coating adhesion of different particle sizes on grit blasted steel. Standard powders adhere better to glass and fine powders to ceramic and plastic; larger particles fuse to glass but degrade plastics and cause large thermal stresses with alumina substrates (Smyth 1973). Heat, mass and momentum transfer in plasmas (Perugini 1976; Vazquez 1976) and nitrogen absorption by liquid metals from plasmas which contain nitrogen are discussed (Basinska-Pampuch & Gibas 1976).

Powder quality is an important factor for high quality coatings and the following properties must be controlled: particle shape and size, size distribution, surface roughness, powder flow ease, composition and homogeneity, melting point, density, moisture content, contamination (Nelson 1973; Kvernes 1983). The gel process of powder production eliminates variations of density and homogeneity. The preparation of powders for plasma spraying is described (Nelson 1973), including the gel process for spherical particles of a specified size in the range 1 to 100 microns. The spherical form ensures a freely flowing powder even at <10 microns diameter and produces a very smooth coating surface. Particles finer than 5 microns tend to agglomerate in the plasma torch feed unit. Porous coatings if required are obtained from coarse powders, the maximum particle size being 0.1 mm. Big particles will penetrate to the flame centre but small ones will not enter the flame at all. Too small particles will oxidize or evaporate and too large ones will only partially melt and may initiate coating cracks. A small range of particle sizes is desirable. Some ceramic powders are hygroscopic and cannot be sprayed beyond a certain moisture level. Preheating before spraying is recommended.

The powder manufacturing process has a great influence on the chemical transformation which occurs during atmospheric plasma spraying. Cobalt coated WC powders and agglomerated sintered powders have been observed to undergo less decarburization during plasma spraying. WC+20%Co coated powder produced the best compromise phase composition and hardness in deposits. Mixed carbide formation was a feature, viz. Co_6W_6C. LPPS at 60 torr produced dense deposits of carbide grains in a cobalt matrix (Vinayo et al 1985).

Plasma spraying can be used for remote repair, e.g. of first vacuum walls of nuclear fusion reactors. But porosity and adherence are problems. Coarse spray particles are advantageous and surface tension lowering by oxygen etc., influences this. Plasma spraying combined with hot isostatic pressing (HIP) improves adhesion. Other combined methods include noble metal electroplating and pack cementation. Low pressure plasma spraying (LPPS) avoids breaking the spray particles by atmosphere collisions. This reduces the time for harmful gas-metal reactions and gives a higher particle velocity (McKelliget et al 1982; Asahi & Kojima 1982). High quality coatings result, e.g. CoCrAlY. Effect of Hf and Y additions has been examined. Plasma spraying Ti in N_2 gives TiN+Ti coatings. High density and hardness is obtainable. Mathematical models of plasma spraying allow parameters which may affect quality to be quantified.

Refractory powders like ZrO_2 can be plasma spray formed into a desired shape on a disposable mandrel or a mandrel precoated with a soluble material (Nelson et al 1973), e.g. yttria-stabilized ZrO_2 electrolyte coatings were produced by the gel process and plasma sprayed directly onto electrodes, or onto a water soluble mandrel to make tubes down to 100 microns thick. Other sprayed artefacts include crucibles for molten metals, furnace radiation shields and tubular resistance elements, mostly useable as sprayed and not needing sintering. The lowest gas permeability was obtained using uniform size spherical particles. The effect of particle size on porosity was determined. Highest density (95%) coatings were given by mixtures of spheres between 10 and 150 microns diameter, due to packing of spheres of different diameters. Loss of Y_2O_3, CaO or MgO cubic stabilizer from stabilized zirconia powder may occur during spraying and more must be added before spraying, which presents problems (Kvernes 1983).

Nearly stoichiometric silicon nitride films (up to 1 micron) were prepared by direct nitridation of silicon in an RF low pressure nitrogen plasma at temperatures below 700°C. The properties of the films were comparable with those of CVD silicon nitride films but uniform layers were however not obtained (Yoshida et al 1982). (Previously silicon nitride films could only be grown by a high temperature thermal nitridation process at temperatures ranging from 1000°C to 1400°C). Nitriding of titanium was performed by rf discharge at 5-20 torr and dc plasma jet at about 200 torr. The nitriding rate in the plasma jet was ten times larger than that in the rf discharge (Matsumoto et al 1982).

LPPS Ti coatings have been found inferior to LPAS (low pressure arc spray-ed/ing) coatings. LPAS coatings were lower in hardness and interstitial gas content but had higher bond strength with the substrate (Steffens et al 1985). LPPS of MCrAlY has found wide acceptance as overlay and bond coatings. The advantages claimed by SPS has been given earlier. NiCoCrAlYTa, 0.19 mm thick has been coated by LPPS on MA 6000 for burner rig tests (Smith & Benn 1987). For CoCrAlY the coating hardness rises with substrate temperature, to a maximum at 650°C and then falls. To cancel such effects, the component is heat treated after coating, e.g. 1 hour at 1100°C in vacuum, which also densifies (sinters) and interdiffuses the coating (Nicoll 1984).

$MoSi_2$ coatings deposited by LPPS on Mo suffer transverse cracks because of the difference in linear expansion. The use of interlayers can overcome this problem; vacuum sprayed mullite (Al_2O_3 + SiO_2), at a substrate temperature of at least 1000°C is found suitable. A special nozzle head was used where the powder injection ports are positioned at different locations and different angles in relation to the nozzle axis. Powders with high m.p. were injected at the throat of the nozzle and others downstream at the mouth of the nozzle. Interlayer compatibility to $MoSi_2$ invloves low solubility and low diffusion coefficient for Si and also no reaction with either Si or Mo. In this respect alumina at controlled thickness was found to be the best choice; zirconates, titanates, silicates and spinels were found unsuitable. Improvement in the Mo - mullite bond was achieved by avoiding large and intermediate splats of both mullite and Mo; very fine Mo and $MoSi_2$ spray are recommended. Sputter etching and coating parameters, in brief, are (Henne & Weber 1986):

	Operating Conditions For	
	Sputter	Coating
Burner Power, kW	30	40
Vessel Pressure, mbar	15	20
Plasma gas	Ar+H_2	Ar+H_2
Powder fraction		<20 microns
Spraying Distance		250 mm
Substrate Temp.,		>/ 1000°C
Powder injection		near nozzle throat.

The multiple layer LPPS coat (by hypersonic spraying) on Mo thus was composed of a graded bond coating of Mo-mullite/mullite/mullite-$MoSi_2$ (enriched with GeO_2 for glass formation) (Henne & Weber 1986).

To coat very reactive single metals and alloys vacuum plasma spraying (VPS) is prefered even to LPPS. Mo, Nb, Ta, Ti, and Zr and their alloys can be best handled by VPS. Once again, the quality of VPS coatings largely depends upon the proper optimization of spraying parameters. Sandblasting, sputtering with a negatively polarized tranferred arc at 20 mbar, and, pre-heating the substrate yielded highly ductile and adhesive Ti and Ti5Al-2.5Fe coatings on austenitic and carbon steel substrates. (Lugscheider et al 1987). The substrates were pre-heated and held at 500°C. Typical temperatures can be as high as 850°C during coating (Nicoll 1984). Computer-aided plasma spraying of turbine blades can help to give a constant distance from gun to substrate, rectangularity to substrate and constant scanning speed (Suzuki et al 1982).

TABLE 6 : 11

SOME CHARACTERISTICS OF DEPOSITION PROCESSES

	CVD	**Electrodeposition**	**Evaporation**	**Ion Plating**	**Sputtering**	**Thermal Spraying**
Metal Deposition	yes	yes - limited	yes	yes	yes	yes
Alloy Deposition	yes	quite limited	yes	yes	yes	yes
Refractory Compound Deposition	yes	limited	yes	yes	yes	yes
Production Mechanism of Depositing Species	chemical reaction	deposition from solution	thermal energy	thermal energy	momentum transfer	
Energy of Depositing Species	can be high with plasma-aided CVD	can be high	low 0.1 to 0.5 eV	can be high (1-100 eV)	can be high (1-100 eV)	can be high
Depositing Species	atoms	ions	atoms and ions	atoms and ions	atoms and ions	droplets
Deposition Rate	moderate 200-2500 A/min	low to high	can be very high up to 750 000 A/min	can be very high up to 250 000 A/min	low except for pure metals (e.g. Cu - 10 000 A/min	very high
Throwing Power for:						
a. Complex Shaped Object	good	good	poor line-of-sight coverage except by gas scattering	good, but nonuniform thickness distribution	good, but nonuniform thickness distribution	no
b. Into Small Blind Holes	limited	limited	poor	poor	poor	very limited
Growth Interface Perturbation	yes (by rubbing)	no	not normally	yes	yes	no
Bombardment of Substrate/ Deposit by Inert Gas Ions	possible	no	not normally	yes	yes or no depending on geometry	yes
Substrate Heating (by external means)	yes	no	yes normally	yes or no	not generally	not normally

A review of thermal spraying is given in Table 6:11 and is briefly discussed below (Tucker 1978):

6.5.5. THERMAL SPRAYING - ASPECTS OF COATING PRODUCTION:

6.5.5.1. Entry of Powder into Plasma Stream:

Plasma Coating Torches:- Very important. The ideal location is upstream of the anode, but powder adherence to the nozzle entry or throat and excessive heating occurs. So the powder entry is usually in the diverging position of the nozzle or just beyond the exit. Improvements consist of adjustments of point and angle of powder entry in accordance with its m.p. Alternatively, shock diamonds are generated and powder is introduced a short distance beyond the exit in the region of rarefaction in the plasma stream. Powder must be distributed uniformly in the plasma stream at a constant rate. A variety of powder dispenser designs are available including those based on auger, aspirated flow or fluidized bed.

Detonation Gun:- A pulsed flow of powder is required. Uniform distribution of the powder in the barrel is important and also of the constancy of amount of powder in each pulse.

6.5.5.2. Substrate Preparation:

Plasma Coating Torches:- Not only must all oxide scale and other foreign matter be removed, but all oils, machine lubricants etc., must be eliminated. Virtually all plasma coatings require a roughened substrate.

Detonation Gun:- Grit blasting may not be necessary because the particle velocity itself results in substantial surface roughening.

6.5.5.3. Substrate Temperature:

Plasma Coating Torches:- One of the major advantages of thermal spraying coats is that they may be applied to substrates without significantly heating them. As a result, a part can be fabricated and fully heat treated, without changing the substrate microstructure or strength. During coating deposition a substantial amount of heat is transmitted to the part through the plasma gas and molten powder. Cooling air or CO_2 jets may be used. Normally the temperature does not exceed 150°C.

6.5.5.4. Coating Material:

Almost any material that can be melted without decomposing can be used to form the coating. For mixtures similar m.p. and b.p. and particle sizes should be used. Also, the difference between m.p. and b.p. of a single phase powder should not be too small, in order to prevent vaporization. Pre-alloyed powder may be better. Comparison of the relative heating rates is not as simple as comparing their m.p. Heat transfer in the plasma jet is primarily the result of the re-combination of the ions and association of the atoms in diatomic gases on the powder particle surfaces and absorption of radiation. Metals tend to heat much more rapidly than most refractory ceramics.

6.5.5.5. Shielding:

This is to stop or reduce the reaction of the powder with O_2 or N_2 from the air inspirated into the plasma stream after it emerges from the nozzle. This is done by an inert gas cloud that surrounds the effluent with argon.

6.5.5.6. Angle of Deposition:

Plasma Spraying Torch:- Plasma deposition is a line of sight process in which the structure of the coating is a function of the angle of deposition. Normally coatings with the highest density and bond strength are achieved at a 90^o angle of deposition. This limitation may cause some problems in coating complex parts, particularly those with narrow grooves and sharp angles.

Detonation Gun:- The D-gun with its higher particle velocity can usually tolerate a wider deviation from 90^o.

6.5.5.7. Size of Equipment:

Plasma Coating Torches:- The smallest torch available until 1980 could apply a metallic coating to a 3.1 cm or a ceramic coating to a 4.35 cm inside diameter at 90^o. Another torch design with an outlet at 45^o to the torch axis, can apply a coating to the inside of a closed cylinder 4.35 cm diameter. Other designs in plasma torches are available.

Detonation Gun:- The D-gun cannot fit into a cylinder or any other type of cavity. It can be used however, to coat an inside diameter to a depth about equal to the diameter, i.e. angle of deposition about 45^o. The inherently high density and bond strength still allows superior coatings to be deposited at lower angles.

6.5.5.8. Masking:

Plasma Coating Torch:- For low velocity , long standoff plasma torches, tapes, oxide loaded paints or stop-off lacquers may be used. For high velocity, short standoff torches, glass fibre reinforced high temperature tape, adhesive backed steel, Al-foil, or sheet metal masking is necessary.

Detonation Gun:- Metal masking is required.

Nicoll (1987) has presented an updated review on thermal spraying equipment and quality control.

6.6. OTHER DROPLET TRANSFER COATING METHODS

6.6.1. COATING BY DETONATION GUN (D-GUN)

D-gun spraying is a form of thermal spraying which consists of heating and directionally propelling powder particles onto the workpiece from a combustion chamber by a stream of gas detonation products. It offers the following advantages:

1. D-gun equipment is relatively simple in design which is both dependable and has a reasonably long service life, unlike, for instance, plasma-arc devices.

2. Low porosity and high bond strength coatings are produced.

3. Substrate pre-treatment is not very stringent. The process is impurity tolerant.

4. With only a moderate substrate heating during deposition a strong bond can be achieved.

5. The powder velociy to temperature ratio has a wider choice and is flexible.

6. There are several means of controlling the thermal cycle of the coating being deposited unlike in other thermal spraying methods.

7. The method enables a high rate of growth of coating thickness.

Inherent deficiencies of the method are:

1. The spray coating process is cyclic and this impedes stabilizing and monitoring the production.

2. Environmental isolation and personnel safegauards are absolutely necessary because of the high noise level.

3. The detonation products are complex and reactive with a number of the components and constituents. CO_2, CO, H_2O, H_2, O_2, N_2 gases and radicals and atoms such as -OH, H, O, NO and N and other gases are produced. This situation imposes production res-

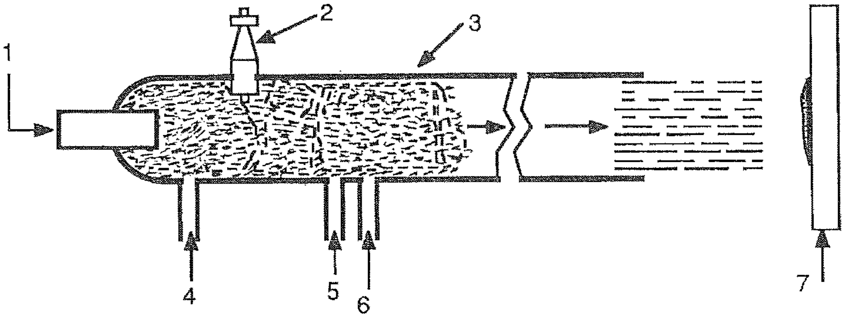
trictions and counter-measures.

4. Distortion of components is a definite possibility. Components to be coated have to be strong enough to sustain D-gun spray impact.

5. The flow from the gun is a two-phase stream. Workpiece to gun configuration is complicated for contoured substrates.

A comprehensive review on D-gun technique is provided by Kharlamov (1987) with references to work from the U.S.S.R.

Union Carbide Corporation (U.S. Patent 2714, 1955) developed a water cooled barrel about 1 metre long with inside diameter 2.5 cm. (Steffens 1983). A $C_2H_2 + O_2$ mixture is fed in with a charge of powder. Metered quantities of oxygen and acetylene are fed via poppet valves into the combustion chamber. Powder in a N_2 stream is metered from a heated pressurized vessel and admitted to the combustion chamber. A spark plug ignites the mixture. The explosion accelerates the powder to 720 m/s and melts it. The 4200°C detonation flame temperature melts most materials. The particle velocity is much higher than with plasma spraying. There are 4 to 8 detonations per second with N_2 purges between each. A 25 mm circle of coating is deposited by each detonation, several microns thick and composed of many overlapping lamellae. The complete coating is made by overlapping many such circles (Tucker 1978). The flame can be oxidizing, carburizing, or inert by precise control. Carburizing conditions can be used to advantage (Price et al 1977). Inert gas shielding is essential for MCrAlY coatings, to stop oxidation during deposition. Fig.6-16 (Tucker 1978) shows a D-gun schematic diagram. A discussion of physical properties of D-gun coatings appears in Chapter 7.



1. Powder injection 2. spark plug 3. gun barrel 4. nitrogen input
5. Acetylene injection 6. oxygen input 7. substrate

Fig.6-16: Schematic diagram of a detonation gun

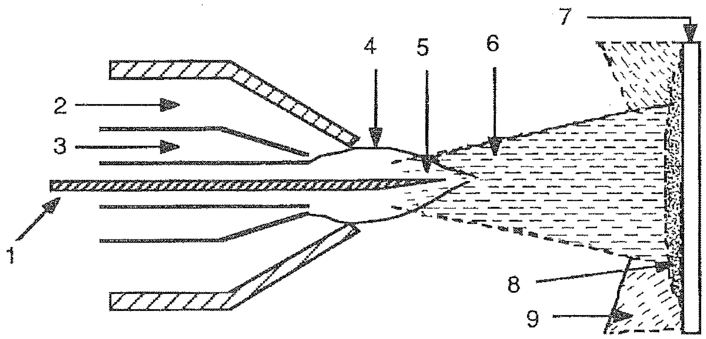
All plasma and D-gun coatings have some open porosity which allows attack by corrosive environments and especially if a molten salt is allowed to freeze. Porosity is reduced by sintering, essential for MCrAlY coatings for gas turbine use. D-gun coatings have less porosity and may not need such sintering (Tucker 1978) as the particle kinetic energy is 25 times greater than in flame spraying. The D-gun hardness is 1300 V.P.N. for a WC/Co coating but only 700 for plasma spraying and less for flame spraying. D-gun bond strengths are very high, and greater than for plasma sprayed coatings (Steffens 1983). Detonation gun coating of Ni and other powders gives highly bonded and dense coatings (Samsonov 1973).

6.6.2. FLAME SPRAYING

Thermal barrier coatings are most often produced by spraying techniques. Flame spraying of ceramics, e.g. zironia + alumina for rocket nozzle coatings, alumina for MHD generating channels, zirconia for jet engine combustion chambers and gas turbines and Cr_3C_2 for gas turbines, is reviewed (Arata et al 1983). Present requirements include development of testing methods, improving adhesion and inter-particle bonding and reducing porosity.

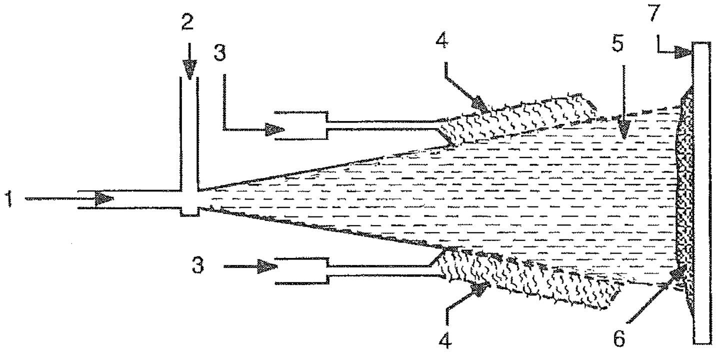
A wire or powder feed of the coating material is fed through an oxy-fuel gas, e.g. C_2H_2 or C_3H_8 flame (Fig.6-17a,b; Tucker 1978). The wire is fed at a controlled rate which allows its tip to melt and to be blown off by the fast flowing compressed air. Wire flame spraying is viewed to be more economical than a powder feed, viz. Fig. 6-18. However, powder feed operation has been developed to more sophisticated levels in recent years and should prove its advantage over solid material feed (Crawmer et al 1987). Coating thicknesses range from about 50 microns upwards (Steffens 1983). Uses include corrosion protection at ambient and high temperatures, rebuilding worn parts and providing wear, abrasion and erosion resistance (Brit. Std. 03-011). Flame sprayed thermal barrier coatings are used in gas turbine engines. Inert gas can be used instead of compressed air, for shielding from oxidation, and the substrate can be independently heated, to obtain better adherence.

Flame sprayed coatings have a much higher percentage of porosity than D-gun coatings (0.25 to 1%). Advanced plasma torch coatings have porosities close to those of D-gun coatings. Flame sprayed coatings contain many round particles (i.e. not lamellar) which are not molten on impact (Steffens 1983). Porosity of flame sprayed coatings can be reduced by vacuum impregnation but only about 0.1mm is permeable by the resin. Atmospheric brushing with resin gives only 0.02mm permeation (Arata et al 1982). A new impregnation method is required, perhaps with a suitable molten salt. LSM is an attractive alternative for deposit consolidation.



1. Feed wire introduced at central axis with wire feed coil-roller configuration 2. Input of compressed air 3. Mixture of oxygen & combustion gases 4. Flame 5. Wire tip 6. Spray cone 7. Substrate 8. Coating deposit 9. Loss of spray material

Fig.6-17a: Flame spraying process - wire form : schematic diagram



Main driving gas injector 2. powder feed nozzle 3.fuel gas injector channels 4. burning gases 5. spray cone 6. deposited coating 7. substrate

Fig.6-17b: Interior of a Flame Sprayer Employing Powder Feed

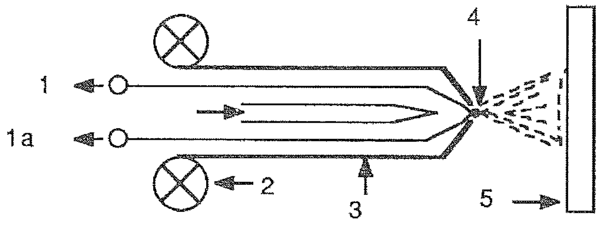
A Ni-Al composite wire generates extra heat in the flame due to exothermic reactions and the resulting coatings are more adherent and less porous than the usual flame sprayed coatings. Cine films have shown these particles becoming hotter as they leave the flame (Hebbert 1978). Details of the exothermic effects of Ni_3Al and Al_2O_3 formation are discussed (Knotek et al 1973; Houben & Zaat 1973). NiAl coatings on steel are described.

Flame sprayed yttria stabilized zirconia coatings on plasma sprayed bond coats of Co32Ni21Cr7.5Al0.5Y and NiCrAl, and arc sprayed 80Ni20Cr were tested for thermal shock (Steffens & Fischer 1987). Microstructure characterization procedures have been attempted and further quantitative correlation to the ceramic oxidation is required. Flame sprayed composites of nichrome and WC were tested for wear and corrosion. Four concentrations of carbide, viz. 85, 55, 15 and 5% were prepared. The wear rate was influenced by both the carbide agglometate and distribution in the nichrome matrix (Olivares & Grigorescu 1987).

6.6.3. ELECTRIC ARC SPRAYING

Two feedable wires are made electrodes for a d.c. electric arc and molten droplets are blown onto the substrate by a compressed air jet (Fig.6-18, Steffens 1983; German Std. DIN 8566). Although similar to flame spraying, the molten droplets temperatures are higher in arc spraying. High speed deposition of thick coatings are readily obtained on large components. Local interface welding is found for Al arc sprayed on steel and in other cases.

Arc spraying does not give as fine a spray as flame spraying. Nozzle design can be altered to optimize the spraying. Spraying wires must be accurately spooled and wear of wire guides causes problems. An attachment is described (Marantz 1973) to allow coating down the bores of long cylinders with diameters of 12cm (or more).



1. D.C. power source; 30 V, 300 A
2. Wire feed - drive and reel
3. Wire
4. Arc
5. Substrate

Fig.6-18: Principal features of an electric-arc spraying process

The adhesion of arc sprayed coatings is stronger than flame sprayed coatings, although the particle velocities are 100 and 180 m/second, respectively. The arc spray particle size is greater and temperature higher, causing local welding. But excessive heat increases shrinkage strains in the coating and burns out alloy constituents, which do not occur with flame spraying. The arc temperature is 6100K with 280 amps (Steffens 1983).

Pseudo alloy coatings are obtained by feeding different wires through each electrode. Thus a 2 phase alloy of Cu and stainless steel can be produced, giving a high wear resistance (due to the steel) and a high thermal conductivity due to the Cu (Steffens 1983). Electrical discharge machining (EDM) coating of steel by Cr, W, Ti and Ni is reported (Parkanski et al 1983). The high density of crystal lattice defects during spark discharge prevents removal of heat which then accumulates within the surface coating layers.

6.6.4. WIRE EXPLOSION SPRAYING

Faraday first obtained very good coatings by wire explosion over a century ago. Wire explosion spraying of W, Mo and piano wire onto Al and steel have adhesion 5 times stronger than by flame spraying (Suhara et al 1973), due to a welded zone between coating and substrate. This occurs because of high velocity and temperature. Applications include spraying Mo inside Al alloy cylinders of internal combustion engines, which is superior to the usual Cr plating. The inside face of glass tubes have been Al coated by this method. Smooth WC-Co coatings are obtainable.

In the optimum wire explosion (Suhara et al 1974,1973,1970) the wire vapour reaches the substrate, rather than just a spray of liquid droplets. This excludes air so that the subsequent shower of W and Mo can be wire explosion sprayed without oxidation. The droplets are spherical and only about 2 to 3 microns diameter. They travel at about 600 m/second. About 60% of the weight of the orignal wire is deposited on a hollow cylinder inner face. The inner surfaces of tubes of diameter as small as 1 cm can be sprayed. The coating thickness is 5 to 15 microns from a single spraying and can be built up by repetition. The coating is smoother and more adhesive than by flame and plasma spraying. The wear resistance of the W and Mo coatings is high and the friction small.

6.6.5. LIQUID METAL SPRAYING

The Osprey metal spray process can be used for building up very thick, e.g. 5 cm, metal coatings in a very short time (minutes). The coating metal is induction melted and atomized by an inert