High Temperature Materials and Processes, Vol. 7, Nos. 2 & 3, 1986, 107-121

A Comprehensive Review on the Development of Ceramic Coatings for Thermomechanical Applications

M.H. Van De Voorde*, M.G. Hocking** and V. Vasantasree**

**Petten Establishment, European Economic Community*
***Imperial College, London.*

CONTENTS

ISSN 0334-1704

ABSTRACT

Ceramic coatings tend to be brittle and devitrefy or spall on thermal cycling, but offer excellent resistance to oxidation and corrosion. Processing methods and the resultant coating microstructures are described. Degradation modes and testing methods are discussed. The following areas are identified for further research: phase diagram and diffusion data, adhesive energy and friction data, adhesion interlayers for ceramic-to-metal coatings, multilayer coating formulations, barrier layers to stop siliciding of substrates, self sealing coatings, lower temperature CVD processing, adhesion and interparticle bonding improvements for flame sprayed coatings and lower porosity, prevention of microchipping of ceramic coats, factors influencing stress in coatings, effect of debris impact, grit inclusions and surface embrittlement, development of shear adhesion tests, thicker and more strain tolerant ceramic coatings.

INTRODUCTION

The application of ceramic coatings to metallic components has gained major impetus during the last decade as the development of metal alloys for increasingly severe service environments becomes technologically and economically less cost effective. The intrinsic properties of ceramics confer advantage to the component in three specific directions:

- wear resistance
- corrosion resistance
- low heat transfer.

This presentation reviews the current status of these coatings for applications requiring the above properties, drawing attention particularly to problem areas and identifying future research needs, and includes an extensive literature survey of progress in the field to date.

Wear resistant coatings are currently operating successfully in static components, such as combustion liners, but require more research before becoming fully applicable to moving parts. Hard overlay coatings, mostly carbides, nitrides or borides have shown greatly reduced wear rates in both adhesive wear and impact erosion compared with conventional chromium plate hard surfacing. Examples include TiN, TiC and Ti(CN) on steel ball bearings and on pistons and valves /1-3, 5/.

Similarly TiB_2 has been successfully applied to Fe-alloys /4/.

Problems arise from the normal CVD processing route which requires heating the substrate to above 800°C, i.e. too high for steels and many alloys. Some success has been achieved at lower temperatures, e.g. W_2C and W_3C, deposited at 300 to 700°C onto steels /6/ although their performance is less than TiC.

Coatings applied by PVD /7/ also show good resistance to abrasive or impact wear, so that chromium carbide and nitride coatings give 4–8 times improvement on conventional hardening by Cr plating while TiC is 34 times better.

For rubbing seal applications self-lubricating surfaces are needed, e.g. in gas turbine engines which need low friction and low leakage rates, combined with corrosion and thermal shock, wear and fatigue resistance. To date, multicomponent coatings such as 85 NiO + 15 CaF_2 /8/ have shown the best prospects. Essential to these coatings are the associated studies of adhesion and friction effects and the development of lubricants or barrier layers as for example Y_2O_3.

Coatings for *erosion/corrosion resistance and thermal barrier* applications face major problems related to coating/substrate stability at high or variable temperatures.

These coatings are required for high thermal flux applications, where, by virtue of low thermal conductivity they allow the substrate alloy (normally cooled) to operate at a temperature far below that of the gas flow.

High thermal gradients and different expansion coefficients give major problems of adherence, which are alleviated only by the application of ductile interlayers between coating and substrate.

The problem is attacked by:

- development of coating-interlayer-substrate systems
- development of coating deposition techniques.

Crucial to the development of stable, elastic interlayers, are studies of metal-ceramic interfaces. The fundamental thermodynamics involved has been reviewed /9/ and several candidate systems evaluated. Of these, adhesion oxides (CuO or MnO) or Ni are often used as an interlayer. Studies of adhesion promoters are needed for all metal-ceramic coating systems. Accumulation of hydrogen at the interface (from H_2O reduction) causes a problem. One solution has been to introduce Ni at the interface which catalytically atomises H_2, so promoting its diffusion away into the steel; the role of adhesion oxides may be to stop the H_2O reduction. Flame sprayed interlayers may improve adherence /10/. The poor tensile behaviour of ceramics and reactions of SiC coatings with NiCrAl are reported at 700–1150°C /11/. Interlayers are needed to prevent eutectic formation at above 700°C. Barrier layers are needed to prevent metal silicide formation (from silicon-containing coatings) at the metal/coating interface. Sandwich joints of Si_3N_4/Zr, Nb, Zr/Si_3N_4 have been made /12/ at 1150°C to study crack growth due to stress; below 900°C adherence does not occur. The adhesion of plasma sprayed ceramics to metals is generally poor but can be considerably improved if a bond-coat or interlayer is used (e.g. NiAl, Mo) /13/.

Recently the protection of metals by ZrO_2 layers has shown major promise /14/ while very good adhesion has been shown by the multilayer system $MoSi_2$-Mo-Ni steel /15/.

An even more innovative answer to the fundamental problem of generating elasticity in the interlayer has been the advent of self-sealing ceramic coatings /16/. Here, the sprayed coating has an open porosity to accommodate elastic strain. The surface, however, is sealed by reaction with the environment giving compressive surface stresses. The underlying layers form a graded bond to the substrate. Fracture of the outer ceramic layer leads to exposure of underlying chromium, further reaction and resealing. Tensile and shear strengths > 3 kg/mm^2 and bending angles of 5° are reported without detachment /16/. Plasma sprayed 'self-sealing' composite coatings of a brazing material (Cu-Ni- etc.) Cr and ZrO_2 are described, and bend testing showed no cracks or coating detachment /17/. Strength values are higher than for other types of powder plasma-sprayed coatings. Further research is needed on such self-sealing types of coatings.

PROCESSING TECHNOLOGIES

Only some of the many coating methods are suitable for ceramic coatings because of the need to maintain stoichiometry in the deposited coating.

Activated Evaporation

Use of a plasma gives the activated evaporation technique which was recently reviewed by Bunshah /18/.

(i) Reactive Evaporation

This process was developed 20 years ago /19, 20, 21/ for the deposition of thin films of compounds at low deposition rates and is the same as in direct evaporation except for the presence of a reactive gas in the chamber. Due to the fact that the partial pressures of the reacting species are low ($< 10^{-5}$ torr) and the mean free path therefore longer than the source-to-substrate distance, reaction between the metal atoms and the gas atoms occurs only on the substrate. E.g.: $2Al(vapour) + 3/2\,O_2(gas) = Al_2O_3$ (solid deposit).

(ii) Activated Reactive Evaporation

This method is used to achieve high deposition rates of compounds /19, 22, 23/. The partial pressure of metal vapour and gas atoms used is $> 5 \times 10^{-4}$ torr. At these pressures the mean-free-path is smaller than the source-to-substrate distance and collision of the reacting species occurs in the gas phase. This could lead to non-stoichiometric compounds /19, 22, 23/; however, by activating the metal and gas atoms, the reaction probability on collision is increased leading to compound formation with the desired stoichiometry. E.g.: $Ti + C_2H_2 = TiC + H_2$ where the carbon/metal ratio of TiC can be varied /19, 22, 24/. Ti evaporated from a rod-fed source by an electron beam was reacted with C_2H_2 (at about 10^{-3} torr) between source and a Ta substrate at 400 to 1000°C /25/. The deposition rate was 1 to 3 microns/minute and the Ti:C ratio was 0.8 to 0.9. A very fine grain structure was obtained at below 700°C, and coarse above that temperature, of similar hardness. Evaporation of V-Ti in C_2H_2 to give VC + TiC was also studied /25/. The molten metal, heated by a high acceleration-voltage electron beam (thermionic electron beam gun) has a plasma sheath on top of the ppol. The low-energy secondary electrons from the plasma sheath are pulled upwards into the reaction zone of an electrode placed above the pool biased to a low positive dc potential (20–100 V). The low-energy electrons have a high ionization cross-section thus ionizing or activating the metal and gas atoms. Variations in the basic ARE process are discussed /26, 27/.

Microstructure of Evaporated Coatings

The important parameters are:

1. Nature of substrate

The evolution of a deposit can start either by the formation of 3-dimensional nuclei on favoured sites on the substrate followed by lateral growth and thickness or a continuous film is formed from the start with no island growth. The first mode occurs where there is poor interaction or bonding between the coating and substrate and the outward growth proceeds to produce in many cases a columnar structure. The second mode occurs under conditions where no oxide films are present and in such cases good bonding between the coating and substrate metal occurs.

2. *Temperature of substrate during deposition*

Increasing substrate temperature has the effect of increasing the mobility of the coating atoms on the surface, thus promoting diffusion /28/. The kinetic energy of the incoming atoms can be increased by partially ionizing the vapour flux and this can lead to epitaxial growth /29/. In this case, the effective surface temperature of the growing film is much higher due to ion bombardment. Movchan and Demichishin /19, 30/ studied the variation of microstructure with deposition temperature for Ni, Ti, W, Al_2O_3 and ZrO_2 and proposed a 3 zone model of structures. At low temperatures, the coating atoms have limited mobility and the structure is columnar, with tapered outgrowths and weak open boundaries (zone 1). If the substrate temperature (T1) is increased above 0.3 of the melting point (Tm) (in °K) of the coating material, then although the structure (Zone 2) remains columnar, the columns tend to be finer, with parallel boundaries, normal to the substrate surface. T1 is 0.3 Tm for metals and 0.22–0.26 Tm for oxides. These boundaries are stronger than in the Zone 1 structure and contain no porosity. At a substrate temperature (T1) above 0.45 of the melting point (Tm) of the coating material the structure (Zone 3) shows an equiaxed grain morphology. Zone 2 structures are associated with enhanced surface diffusion and Zone 3 structures with bulk diffusion. Zone 3 is not seen very often in materials with high melting points.

3. *Surface roughness and incidence angle of the vapour stream*

Since evaporation is primarily a line-of-sight process, the effect of any asperity or projection on the surface will be increased when the vapour stream is at a low angle to the substrate surface. Leaders are columnar defects which are poorly bonded to the rest of the coating and result from localized rapid growth due to shadowing effects caused by surface protrusions. Specimen rotation results in improved as-deposited coating quality.

4. *Gas pressure*

High gas pressure during deposition inhibits surface mobility and hence can be the cause of columnar structures even at elevated temperature. The model proposed by Movchan and Demchishin was extended by adding an additional axis to account for the effect of gas /31/ and was subsequently modified by Thornton to account for an additional transition zone (Zone T). This was identified between Zones 1 and 2. Zone T is a columnar Zone 1 structure with small crystal sizes that appear fibrous and with boundaries that are sufficiently dense to yield good mechanical properties.

Ion Plating

This method is reviewed by Mattox and others /32-39/. Ion plating is good for wear and erosion resistant coatings, due to its good adhesion characteristic, e.g. HfN for low friction and TiC for deformation and bonding resistance /40-41/. For an incompatible coating and substrate, ion plating can be used as a "strike" for electroplating.

The very good adhesion of ion plated coatings (much better than vacuum evaporated coatings) is attributed to the high energy of deposition /40/. Ionisation energy effects modify the coating structure /41/, similarly to the effect of substrate temperature in the Movchan and Demchishin model.

Sputtering

Stoichiometry problems occur. The changes in characteristics of TiC and TiO_2 coatings by a magnetron-sputtering process onto Mo etc., was investigated /42, 43/. Without Ti addition, the deposited films were excessively rich in carbon.. The stoichiometric or Ti excess films deposited with Ti addition were more resistant to thermal cycling. The films containing large amounts of Ar deposited with Ti addition were apt to form blisters and exfoliate during the heating tests.

CVD and metalliding often require process temperatures exceeding the steel substrate tempering temperature and for coating inside steel tubes sputtering is adaptable to tubular geometry and requires lower substrate temperatures. Atomic cleaning by intense ion bombardment before sputtering Ta and Mo in low pressure Kr is successful, at 0.6 microns/minute. Adherent dense coatings resulted /44/.

Sputtered Coating Morphology

The nucleation and growth of sputtered coatings is similar to vacuum evaporation, although the pressure is much higher. The sputtered atoms reach the substrate with about 10 to 40 eV kinetic energy, compared with 0.3 to 1 eV for vacuum evaporation /41, 45/.

The higher gas pressure lowers the temperatures defining the zone boundaries in the Movchan and Demchishin diagram and so a higher temperature is needed to produce a dense structure /41, 45/. Further research is required.

Some compounds can be sputtered from compound targets, but the stoichiometry may change /41/. Use of a reactive gas allows deposition of Al_2O_3, TiN and CdS, for example (called Reactive Sputtering). The rate is usually low because the reactive gas poisons the target surface /41/. Using several targets sequentially creates a layered coating /45/. The substrate temperature can be independently varied to get the best coating microstructure. Ion bombardment while sputtering improves throwing power /46/.

CVD

Yee /47/ and Blocher /48/ have reviewed CVD and tabulated many carbide, nitride, boride and oxide coatings obtained from suitable volatile reactants. The subject is too diverse to discuss here but has proved highly successful for many applications such as carbide coatings for machine tools. The problem is that the substrate temperature may need to be about 800°C which alters the mechanical properties of steel.

Slurry Coating

Apart from metals and alloys, ceramic coatings have also been applied /49/.

Electrodeposition from Melts

Adherent tantalum carbide coatings on nickel substrates are obtained from a ternary (Li-, Na-K-) fluoride eutectic containing K_2TaF_7 and K_2CO_3 at 750–800°C. Ta and C are simultaneously discharged and react at the Ni-electrode to result in abrasion resistant TaC coatings stable up to 600°C /50, 51/. Cermet coatings can be electrodeposited /52-54/.

Coating by Plasma Spraying

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. Frequent problems with plasma sprayed coatings are porosity and poor adhesion. Special care is needed, as in electroplating, to clean and prepare the surface to be coated /55-62/. The substrate temperature may reach only about 200°C, in contrast to CVD which gives much higher temperatures.

In given plasma conditions there is likely to be an optimum power particle size which will be melted and transported with enough momentum. Powder size affects adhesion and porosity /63/. Coatings 3 microns thick are got from metal powders 1 to 5 microns diameter. 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 /64/. Flame spraying of ceramics, e.g. zirconia for jet engine combustion chambers and gas turbines and Cr_3C_2 for gas turbines, is reviewed /65/. Present requirements include development of testing methods, improving adhesion and interparticle bonding and reducing porosity.

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 not obtained /66/. (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 /67/.

D-Gun Coating

D-Gun coating can provide carburizing conditions if required during coating /68/. Highly bonded and dense coatings can be obtained /69/.

Other Methods

Sol-gel coating /70, 71/ has been used for ceria, silica, zirconia, titania and alumina. But little has yet been published on properties except for their oxidation resistance. Laser cladding of Al alloys with alumina applied as a loose submicron powder and of carbides has been reported /72, 73/. Diffusion bonding is an excellent method of ceramic coating /74-76/.

FACTORS INFLUENCING AND CONTROLLING DEGRADATION

The deterioration of a coating and its eventual failure is primarily linked to: (i) the process by which it is applied, (ii) its metallurgical compatibility with the substrate, and (iii) the joint response of coating plus substrate to the operating environment.

(i) The Coating Process

Faults in 4 aspects of coating processes can initiate coating failure: Coating composition, nucleation and build-up; Coating/substrate bonding; Coating thickness and uniformity; Coating defects (e.g. pores).

Ceramic coatings often spall due to transient thermal stresses, failure occurring within the ceramic, near to but not along the ceramic/metal interface /77/. A metal felt between the metal substrate and the ceramic coating helps to accommodate shear stresses due to thermal expansion mismatch /78/.

(ii) Problem Areas in Substrate-Coating Compatability

Several problems occur at the process stage which affect the coherence of the resultant substrate-coating complex. These are caused by: Intermetallic compound formation; Diffusion; Interdiffusion; Effect on ductile brittle transformation temperature; vaporization, selective attack, mechanical strain and creep effects, effects on microstructure and phase formation, and thermal shock and fatigue.

Degradation of Thermal Barrier Coatings

ZrO_2 (MgO or Y_2O_3 stabilised): Vanadates (from diesel fuel combustion) attack the MgO or $Y_2O_3 \cdot SiO_2$ on 9Cr-steel: Cracks due to mechanical strain allow oxidation in CO_2. $ZrO_2-12\%Y_2O_3$/Ni16Cr6Al·6Y duplex coating on superalloys: salt melts absorbed by coat porosity and then thermal shock failure follows; acid fluxing hot corrosion mechanism also occurs.

Failure of thermal barrier coatings can be initiated by poor bonding to the substrate matrix, or the coating parameters such as porosity, microstructure-microcrack distribution, thickness, phase distribution and cohesive strength, or the relative thermal expansion and residual stress of the substrate-coating system /79/.

With the failure criterion defined as surface cracking visible under X 10 magnification, an oxidation based model has been developed for predicting ceramic barrier coating life. The model is based on the cumulative effect of oxidation and thermal cycling on strains which promote crack growth. The model fails where more complicated reactions are involved, and is also vulnerable to variations in coating characteristics during coating production /80/.

Thermal fatigue failure is common in ceramic coats. The first rule-of-thumb order may be postulated to be that a coating should have 1–2% ductility at the temperature of occurrence of maximum strain, and should have enhanced thermal fatigue resistance compared to elastically brittle coatings /81/. Ceramic coats spall due to transient thermal stresses aggravated by salts which induce hot corrosion.

Coatings of Si_3N_4, TiB_2 and Al_2O_3 proved to be effective barriers when free of fissures and pinholes /82/. Self-fluxing alloys of Ni-Cr-Si-B have great oxidation resistance. These are arc-sprayed from wire or powder stock, and surface oxidation of the particles (which would prevent coalescence) is removed by the B and Si to give a fully dense fused deposit, also cleaning the base metal. However, if the substrate is Cr-rich, its oxidation occurs unless spraying and fusing are simultaneous.

Titanium carbide and nitride are well-bonded to superalloys if the Ni_3Ti intermetallic phase is controlled. An excess produces a rough deposit and thus a poor bonding. A marginal carburization is also a requirement for good bonding /83/.

Without an interlayer, ceramic-substrate interactions are inevitable, and also thermal cycling will debond the coating /84, 85/. MgO, Al_2O_3, SiO_2 (as fused quartz), SiC and Si_3N_4 were all found to react with a Ni-based superalloy substrate, the most severe being Si-SiC at over 700°–1150°C, with conditions at the interface held at minimized pO_2. Si and C diffused inwards forming silicides and carbides, with the degree of reaction on the ceramic side being similar to that of the substrate below 900°C, and less above 900°C /86/. Plasma sprayed magnesia-stabilized zirconia (MSZ) thermal barrier coating over a mixed MSZ + NiAl coating over a thin NiAl bond coat has been used in gas turbine combustion chambers /87/ but oxidation of the NiAl occurs. Better bond coats are NiCrAlY and CoCrAlY which resisted hot corrosion. The best ceramic overcoat was 8% yttria-stabilised zirconia, which did not peel or spall /87/ in molten salt tests at 800°C in 11 ks or in 1000 cycle 400°C to 900°C burner rig tests. The substrate was Hastelloy X or Haynes 188.

Chemical and thermal-mechanical interactions are cited for the failure of porous, plasma-sprayed ZrO_2-Y_2O_3 (8, 15, 20 wt%), ZrO_2-MgO (24.65 wt%) and Ca_2SiO_4 with NiCrAlY as a bond coat on U-720 and ECY 768 alloy samples. Fuels ranged from pure diesel GT no. 2 to doped 1–100 ppm Na, 2–180 ppm V, 2–18 ppm P; 0.25–2.25 wt% S impurities. Partially stabilized ZrO_2 containing small fractions of monoclinic ZrO_2 out-performed fully stabilized ZrO_2. The 2-phase ZrO_2 could develop micro-fissures to relieve thermal stresses. In vanadium and sea salt-contaminated fuels graded coatings of NiCrAlY bond coat/NiCrAlY-oxide graded zone/oxide overcoat were better than a duplex NiCrAlY bond coat/oxide overcoat /88/.

Unlike in the oxidation-hot corrosion area, the failure mode of ceramic coats used for wear resistance is via micro-chipping. Cemented carbides such as TiC, TiC_xN_y and TiN degenerate with abrasive excursions and impact. The ceramics fail by transverse crack development, TiC being superior to TiN /89-91/.

Strain and Thermal Cycling

Thermal expansion is the commonest source of mismatch strains, especially important for ceramic coatings. The thermal expansion coefficient of ceramics is about 8×10^{-6} K^{-1} and steel is about 14×10^{-6} K^{-1} and a thin intermediate layer of oxide and metal can be used to reduce interface mismatch strains /92/.

Transformation strains depend inversely on the degree of stabilization in ZrO_2 and may counteract some of the thermal expansion strain /92/. Microcracking due to a phase transition or porosity may relieve thermal mismatch strains /92/.

A successful diesel engine coating for thermal shock resistance is MgO + ZrO_2 on a NiCrAlY bond coating /93, 92/. MgO·ZrO_2 has good resistance to wear and flexural fatigue /92/. Ceramic thermal barrier coatings reduce substrate temperatures by 120 to 150°C. Control of porosity, segmentation, microcracking and residual stress, has given rise to great increases in the number of cycles to failure compared with 1977 values. Self-healing plasma coatings (described below) are used on a 2-stroke diesel piston head, subject to thermal shock and sulphur corrosion from the oil. The piston showed no damage after 28,000 hours and 230 million thermal shocks /94/. Self-sealing coatings have an outer layer (e.g. ZrO_2), an intermediate layer (e.g. Cr + ZrO_2) whose porosity is reduced by its oxidation (which also causes mechanical and chemical bonding to the outer ZrO_2), and an inner layer (e.g. Cu-Ni). Recommendations are given /94/.

Thermal Conductivity

A high thermal conductivity increases resistance to thermal shock, while a low value allows higher engine temperatures and adiabatic designs. Thermal and mechanical properties of plasma and D-gun coatings are reviewed by Tucker /95/. As-sprayed coatings can have very low thermal conduction but on heating this can increase greatly due to sintering shrinkage.

The lamellar microstructure of D-gun coatings gives a lower thermal conduction than of the fully dense solid. Thermal barrier coatings fall into 2 types, thin (< 0.02 inches) and thick (up to 0.25 inches). The thin barriers are used in gas turbine engines and diesel and petrol engine piston heads and valves. They are Ni-Cr, Ni-Al or MCrAlY with (e.g.) ZrO_2 or $MgZrO_3$ as a thermal barrier on top /95/. A continuous gradation from metal to oxide can be used for better thermal shock resistance. The metal part of the coating must resist oxidation (since the oxide layer is porous). This continuous gradation is more necessary with thick thermal barrier coatings /95/.

Tensile stress in AlN coatings is due mainly to differential thermal contraction on cooling, but the net stress is compressive /96/ and increases with deposition temperature. Adding Si_3N_4 sharply reduces the net stress and puts it into the tensile region.

Holding MgO-stabilized ZrO_2 above 1000°C allows MgO to precipitate out, causing ZrO_2 instability, and its increasing thermal conductivity can rise to 3 times its previous value. This causes the hottest areas to degrade fastest and needs further reseach.

Yttria stabilized zirconia coatings have a high microcrack density next to their bond coat and are inferior to MgO stabilized zirconia in thermal cycling. A martensitic transformation can occur and, if the sprayed ceramic powder is a phase mixture, the same nominal composition can give 2 orders of magnitude differences in rig test life. To get a single phase (homogeneous) powder for spraying, the sol-gel process is used and greatly improved performance results /97/.

Little research has been done on the effect of impact on ZrO_2 coatings but even mild grit blasting will cause serious damage. Semi-molten debris contracts on freezing and spalls off the coating.

Research is needed on how stresses are generated and transmitted through the coating and how coating production can form more uniform structures.

Typical bondcoat compositions are shown below /98/:

Notes:

1. Bondcoat thickness is normally 180 microns (0.007") and ceramic is normally 250–300 microns (0.01–.012").
2. LTB 13 is processed to produce a controlled micro-crack density.

Designation	Bondcoat Composition					Ceramic Composition		
	Co	Ni	Cr	Al	Y	ZrO_2	MgO	Y_2O_3
LTB 4	23	48	17	12	0.3	75	25	
LTB 5	22	48	20	9	0.5	75	25	
LTB 6	23	48	17	12	0.3	88		12
LTB 7	22	48	20	9	0.5	88		12
LTB 8	39	32	21	7.5	0.5	75	25	
LTB 12	39	32	21	7.5	0.5	93		6.5
LTB 13	39	32	21	7.5	0.5	93		6.5

Adhesion

Poor adhesion can arise at any of the three major stages in a coating process:

1. a. The substrate condition. b. The purity of the coating chemicals. c. The cleanliness of the equipment used.

2. The bonding between the substrate and the initial deposit; deposit growth.

3. The final compatibility of the substrate to the coating in order that the composite piece can function as a unit.

Ceramic coatings have a strain-to-failure $\leqslant 1\%$ and so cannot tolerate substrate expansion. The mechanism of bonding of plasma deposited coatings in many respects is still under review /99-102/. Mechanical interlocking has been considered the most important mechanism by most investigators. It has been shown /103-105/ that bond strength increases with increasing surface roughness in both shear and tensile tests, although it may diminish again above 0.25 to 0.3 mils, rms. Few published reports have taken into account the detrimental effects of surface embrittlement, peak blunting and grit inclusions /106-108/ when excessive grit blasting is used. Bond coats (to hold a ceramic coating on) have different adhesion for the ceramic if CVD or PVD is used and further research is needed in this area. EB PVD bond coats are usually 50 to 120 microns thick, with surface finish 0.2 to 1 micron. The initial ZrO_2 layer deposited on the alumina of the bond coat is dense and columnar and must be kept below about 2 microns thick to prevent stresses due to thermal expansion mismatch. The outer yttria-stabilized zirconia layer must have lower density for strain tolerance.

Most of the factors that affect the bond strength of plasma deposited coatings also apply to D-gun coatings. Because of the unusually high velocity of the particles, they are actually driven into the surface of most metallic substrates. Some substrates require no grit blasting to achieve adequate bonding, since the coating process itself roughens the interface. This embedding/roughening process creates atomically clean interfaces between the coating and substrate over most of the coating area, which facilitates chemical bonding and can be likened to the explosive bonding of sheets of metal. This undoubtedly plays a large role in forming the unusually high bond strengths of D-gun coatings /99/. In some cases holding the substrate at constant temperature (e.g. 300°C) during D-gun spraying can give improved adherence where a large thermal mismatch is present. Some D-gun coatings are so well bonded that a crack starting in the coating may propagate into the substrate on cyclic stressing.

Cohesive fracture toughness of plasma coatings is much less than that of the same bulk material, due to the lamellar structure /109/.

Bond coat interlayers succeed because their metallic lamellae allow plastic deformation; failure near a ceramic/metal interface occurs by brittle fracture between ceramic lamellae or between ceramic lamellae and substrate /109/.

Ion plated coatings have excellent adhesion and resistance to thermal shock and vibration /110/.

Bryant and Meier /111/ discuss the causes of poor adherence of CVD coatings and show that absence of substrate attack by the CVD gases is a necessary factor. Other factors which are often cited are: (i) reaction in the gas phase rather than on the substrate surface which produces a flaky deposit; (ii) formation of brittle intermetallic compounds between coating and substrate; (iii) hydriding of substrate in coating systems containing hydrogen, and (iv) contamination of the substrate prior to deposition, e.g. by the formation of a thin-oxide film.

A low Young's modulus decreases the chance of brittle fracture occurring during deformations. Ceramic coatings (e.g. ZrO_2 + MgO) have a lower modulus than sintered ceramic materials.

Tensile stress in AlN coatings is due mainly to differential thermal expansion on cooling but the net stress is compressive /112/ and increases with deposition temperature. Adding Si_3N_4 sharply reduces the net stress into the tensile region.

Residual stresses cause coating failure. All melt coating processes result in significant residual stresses. Research is needed on the residual stresses in spray coatings.

Research is needed to develop shear adhesion tests as coatings are more often used in shear than in tension /99/. Further work is needed on the bad effects of surface embrittlement and grit inclusions /99/.

Plasma sprayed 'self-sealing' composite coatings of a brazing material (Cu-Ni, etc.), Cr and ZrO_2 are described, and bend testing showed no cracks or coating detachment /113/. Strength values are higher than for other types of powder plasma sprayed coatings and further research is needed on such self-sealing types of coatings.

The microstructure of flame sprayed alumina consists of a series of overlapping lamellae produced by the splat cooling of impinging droplets. Porosities $< 10\%$ can be achieved, with good adhesion /114/. Metastable gamma alumina is formed by flame spraying, not the expected stable alpha form. Flame sprayed bond-coat interlayers of NiCrAl alloy are shown to improve the adherence of SiO_2-Al_2O_3 coatings on Ni-Cr and Co-Cr alloys /115/. Adhesion tests of CoCrAl, CoCrAlY and CoCrAlHf coatings have been reported /116/.

Bond coats (to hold a ceramic coating on) have different adhesion for the ceramic if CVD or PVD is used and further research is needed in this area. EB PVD bond coats are usually 50 to 120 microns thick, with surface finish 0.2 to 1 micron.

The initial ZrO_2 layer deposited on the alumina of the bond coat is dense and columnar and must be kept below about 2 microns thick to prevent stresses due to thermal expansion mismatch. The outer yttria-stabilized zirconia layer must have lower density for strain tolerance.

Creep, Hardness and Wear

Hardening mechanisms of thermally sprayed hard facings such as Ni_3B and carbides have been discussed /117/. Factors affecting wear and wear behaviour and wear resisting coatings are discussed by Child /118/.

PVD wear resistant TiC, TiN and Ti(C,N) coatings onto low temperature substrates usually give poor adherence and film morphology. A low N_2 pressure improves adherence, as do a thin Ti film /119-121/ and vaporization in $C_2H_2 + N_2$ /122/.

Oxide and fluoride films reduce high temperature friction /123/, oxide films having temperature independent friction coefficients.

Requirements for hot wear resistance are /118/: – high hot hardness (resistance to thermal softening) – structural stability (temper resistance) – retention of adherent oxide films to act as lubricants – high thermal fatigue resistance – corrosion resistance.

The improved wear resistance of hard carbide layers is not at the expense of lower fatigue strength /118/. For best fatigue properties, plasma nitriding or vacuum carburising is needed /118/.

Very hard, wear resistant ceramic coatings (e.g. TiN) are obtainable by activated reactive evaporation (ARE), reactive sputtering and ion plating.

CVD TiC, VC, NbC and Cr_7C_3 are used on valves.

30% chromium carbide powder electrolytically codeposited in a Co matrix have excellent wear resistance /124/. These coatings have been successful for gas turbine aircraft engine parts, at 15 to 125 microns. Worn Al alloy pistons can be salvaged by such 250 micron coatings /124/. Wear resistance up to 700°C is given by a Co + Cr_3C_2 cermet coating which provides a hard glaze of Co_3O_4 debris retained by Cr_3C_2 /125/; wear resistance is also partly due to an hcp lattice.

Very high (10 to 20 GN/m^2) hardness at 1500°C is reported for CVD Si_3N_4 /126/.

Erosion-corrosion resistant coatings of TiN and Ti_5Si_3 or $TiAl_3$ on Ti owe their hardness to the nitride, and their oxidation resistance to the silicide or aluminide.

Rubbing seals are needed for ceramic gas turbine regenerators. Requirements are $<$ 25 microns per 100 hours for both matrix and coating and a friction coefficient of $<$ 0.35. Conventional solid lubricants (graphite, MoS_2) oxidise below 500°C. Plasma sprayed NiO-CaF_2 on Inconel 601 were studied at 760°C /127/. Ideally, this type of composite coating with a hard (NiO) matrix containing a small amount of soft (CaF_2) material, will have friction no higher than that of the soft material and wear no higher than the hard material. Friction tests on plasma sprayed coatings are reported /128/. The use of NiO + CaF_2 (plasma sprayed from powders) for coating truck turbine engine heat exchanger seals is described /128/.

Ion implantation of interstitial species like N & C has major effects on surface-related mechanical properties /129-133/. The lattice distortion is analogous to the effect of shot blasting the surface and increases hardness. The relation between wear and oxidation in ion-implanted metals is discussed by Dearnley /134/; ion implanted species on oxide grain boundaries or dislocations block fast diffusion paths. Ion implantation has succeeded where oxidation and stresses coexist.

Plasma and D-gun coatings are mainly used for their wear resistance and this is reviewed /135/. A D-gun coating is usually more wear resistant than a plasma coating of the same composition. The high bond and cohesive strength of D-gun coatings allow their survival to impact, temperature and fretting /136/.

Before deciding which coating to apply for wear resistance it is important to assess the reasons for the wear. Wear may involve mechanical separation of small particles, corrosion, thermal shock or mechanical stress. If due to the scoring action of hard particles, a hardfacing alloy may be suitable. If due to oxidation, a Co-C-Fe alloy (etc.) may be suitable. Co-base alloys give low temperature and high temperature (1000°C) wear resistance. General reviews of wear resistance are available /137-140/.

TESTING AND INSPECTION OF CERAMIC COATINGS

Testing and inspection falls into 4 areas /141/:
– Standard characterisation (property measurement)
– Non destructive testing (NDT) – Screening – Environmental simulation. Test methods include ultrasonics (holography, tomography, CS technique, pattern recognition), acoustic emission, acoustic microscopy and eddy current methods.

The NDT techniques of radiography, eddy current, thermoelectric measurements and dye penetration have been reviewed /141/. Use of fluorescent dyes to find surface cracks and porosity can also be used to find cracks in the visually inaccessible inside surfaces of objects, e.g. inside drilled holes. The method is fast and cheap. As with the conventional dye method, fluorescent dye is spread over the surface to be inspected and wiped clean. A silicon rubber molding compound is then applied to the inner surface and peeled away after curing. Dye that entered any inside surface crack is absorbed by the silicon and will glow under ultraviolet light /142/.

Acoustic Methods

Ultrasonic, acoustic emission, thermal and holographic interferometry are discussed in detail /143, 144/. Acoustic microscopy for characterising PVD films is described. Adherence, hardness and wear resistance can be characterised /145/. Subsurface microstructures and flaws can be detected /146, 147/. The controlled signals (CS) ultrasonics technique uses a modulated carrier wave, the modulation feature allowing effectively about 900 times the acoustic energy of an unmodulated wave /148/.

Accurate images are obtainable by acoustic holography, giving a 3-D picture of any interior fault /149/ but further development is necessary due to high temperature attenuation of high frequencies (5 MHz). Resolution is about one wavelength. Optical holography allows an advantageously large working distance, and a laser image of the surface is combined with a reference image and then compared with the images when the specimen is stressed. Irregularities due to flaws will appear, if near the surface (as in coatings) /147/. Large surfaces can be inspected by this method (several square metres).

Thermal Methods

Conventional NDT (non-destructive testing) using ultrasonic and dye penetrant methods have variable success on thermal spray coatings /150/. Thermal NDT for coatings have been reported /151-153/ but only two included elimination of surface emissivity effects /154, 155/. Thermal wave analysis is an advanced recent method /156-158/. After a transient thermal injection from a gas jet heater, the surface temperature falls due to inward heat conduction which is modified by the coating-to-substrate bond, coating thickness variation, porosity, density and emissivity. An infrared scanner builds up a map of surface temperature which thus shows the condition of the substrate-to-coating bond /159, 155, 156/. A thermoelectric method has been described /141/.

Adhesion tests are described /160-163/.

Wear Tests

A typical wear test machine has rollers touching at different speeds, the roll diameter and weight loss being measured /164/. This is used to select candidate materials for diesel engine testing. Plasma sprayed alloy coatings containing 20 to 30% free graphite gave promising results /164/. Friction and wear of alumina coatings with various pins is discussed in pin-on-disc wear tests /165/. A hammer wear test is more arduous and assesses the coating cohesion and also adhesion /166/. Co + Cr_3C_2 shows good wear properties, nearly matching plasma and flame sprayed Co + WC deposits and equalling plasma sprayed Co alloy X-40 /166/.

Grinding wheel or abrasive powder wear tests of coatings can sometimes indicate the hardness or brittleness of coatings, rather than their wear resistance under the usual conditions of service /160/.

THERMO-MECHANICAL APPLICATIONS OF CERAMIC COATINGS

Gas Turbine

Thermal efficiency improvement and corrosion resistance requires coatings for gas turbine components. Metallic coatings reduce corrosion and ceramic types act as thermal barriers to reduce static component temperatures. The adherence and thermal shock resistance of ceramic coatings delays their use on rotating blades.

Requirements include overlay coating processes for low coat quality coatings, coatings for erosion protection which are compatible with overlay coatings. Requirements for both alloys and coatings are reviewed /167, 168/.

The presence of salt melts prevents use of coatings such as ZrO_2-12%Y_2O_3 on Ni-16Cr-6Al-0.06Y intermediate layer on superalloys, due to absorption of salt in the porosity and subsequent thermal shock failure. Better resistance is obtained with glassy coatings like $2CaO \cdot SiO_2$ or with a MgO-NiCrAlY cermet, on superalloys.

Zirconia coatings are important in the combustion zones of aero gas turbine engines. There is a need to develop thicker coatings or monolithic materials. Further work is needed on production of strain-tolerant ceramic thermal barrier coatings for combustion zones.

Good mechanical properties are reported for some coatings in the series Ni/Al, Ni/C, Co/WC, NiCr/diatomite, Ni/$WTiC_2$, NiCr/Cr_3C_2, Ni/CaF_2 and NiO/CaF_2, on superalloys /169/.

Diesel Engines

Reducing heat losses increases efficiency but raises temperatures. Thus thermal barrier coatings are needed on valves, piston crowns and cylinder heads. To improve efficiency the engine can be operated uncooled (adiabatic engine), requiring thermal barrier coatings such as zirconia. At least 3.5 mm is needed to obtain an 80% heat loss reduction /170/. This is beyond plasma spraying capabilities and thinner zirconia on a metal fibre layer has been suggested /171/.

If cylinder liners are made from a solid ceramic, the piston rings need a wear resistant coating with compatible thermal expansion. Multicomponent plasma coatings can be self-lubricating up to 870°C /172/, e.g. 30% nichrome, 30% Ag, 25% CaF_2, 15% glass (to prevent nichrome oxidation). Ag improves wear properties at lower temperatures (start-up). Stabilized ZrO_2 on a NiAl or NiCrAlY bond coating, graded and up to 0.8 mm thick have performed well on piston crowns of marine diesels using normal fuel. Low quality fuel contains V which reacts with the Y_2O_3 or CaO stabilizers in the ZrO_2 and causes disintegration. MgO stabilizer is more resistant /173/. Large diesel engine piston heads, plasma spray coated with self-sealing ceramic, resisted sulphurous combustion gas attack up to 1500°C under severe thermal shock and fatigue stress /174/.

Braze/cermet/ceramic coatings on steel (AISI-4320) gave very good corrosion resistance with hot wear and thermal shock resistance and good tensile and shear resistance /175/. Cr_3C_2/Mo and Ti-Ni alloy with 3% free C as coatings on piston rings on marine diesel engines showed improved wear resistance compared with grey cast iron /176/. Stabilized ZrO_2 coatings on steel components had big tensile strength differences /177/. Kvernes has recently discussed coatings for diesel engines /178/.

Ceramic Coating Methods – Some Examples

Method	Coating	Type	Rate
CVD	SiO_2, TiSi, SiB, TiN Si_3N_4, and many others /47/	O & D	medium
EBE	Al_2O_3, ZrO_2	O	high
ARE	TiN, TaN, VC, TiC, In_2O_3	O & D	high
PS	Al_2O_3, Cr_2O_3, ZrN, MoS_2, CaF_2, ZrO_2, TiO_2	O	high
FS	ZrO_2, Al_2O_3, Cr_3C_2	O & D	high
DG	WC, Cr_3C_2, WTiC, Al_2O_3, TiO_2, Cr_2O_3	O & D	medium
RIP	ZrO_2	O	medium
SG	CeO_2, SiO_2	O	medium
SL	carbides	O	
RE	Al_2O_3	O	medium
S	TiN, Ta_2O_5, TiO_2, Fe-Cr-P-C, Cr_3B, Ti_3B	O	medium
RS	Al_2O_3, TiO_2, NbN, TiN, CdS	O	medium
IP	TiC, HfN	O	medium
HIP	Al_2O_3, ZrO_2, MgO, SiO_2, BeO	O & D	

KEY: CVD = chemical vapour deposition; EBE = electron beam evaporation; ARE = activated reactive evaporation; PS = plasma spray; FS = flame spray; DG = D-gun; RIP = reactive ion plating; SG = sol-gel; SL = slurry; RE = reactive evaporation; S = sputtering; RS = reactive sputtering; IP = ion plating; HIP = hot isostatic pressing cladding.

O = overlay; D = diffusion bonded. (Note: "diffusion bonded" here includes some diffusion caused by a possibly directly or indirectly heated substrate. This could be applied in other methods listed above and 'D' could be written for most methods listed above).

Some Applications of Ceramic Coatings

WEAR RESISTANCE: TiN, TiC, Ti(C,N), ZrN, TaN, Si_3N_4, WC-TiC-TaC, TaC, BC, BP, ZrB_2, HfB_2, TiZrB, ZrO_2, Al_2O_3, NiO + CaF_2/SrF_2, Cr_3C_2, Cr_7C_3.

EROSION RESISTANCE: Ta_2O_5, TaN, $NiOCaF_2$, $NiCaF_2$, Cr_3C_2, $WTiC_2$.

CARBURIZATION RESISTANCE: NbB_2, TaB_2.

OXIDATION RESISTANCE: SiO_2, Al_2O_3, MgO, BeO_2, HfO_2, Ta_2O_5, CeO_2, Ru, Ir oxides, $NiOCaF_2$, $NiCaF_2$, WSi_2/ZrO_2, $ZrSi_2/ZrSi$, $MoSi_2/ZrO_2$, $MoSi_2$, $NbSi_2$, VSi_2, $ZrSi_2$, $CrSi_2$, $TiSi_2$, Ti_5Si_3, TiB_2, HfB_2, ZrB_2, HfC.

DIFFUSION BARRIER: TiC, TiN.

REFERENCES

1. GASS, H. and HINTERMANN, H.E., *Proc. 4th Intl. Conf. on CVD,* G.F. Wakefield and J.M. Blocher, eds., Princeton Pub. Electrochem. Soc., p. 563.
2. YEE, K.K., *Intl. Met. Rev.,* **23(1),** 19 (1978).
3. TAKAHASHI, T. and ITOH, H., *J. Mat. Sci.,* **14(6),** 1285 (1979).
4. TAKAHASHI, T. and ITOH, H., *J. Electrochem. Soc.,* **124(5),** 797 (1977).
5. HINTERMANN, H.E., *Proc. 3rd Intl. Conf. CVD, Hinsdale IL,* F.A. Glaski, ed., Am. Nucl. Soc., p. 352 (1972).
6. ARCHER, N.J. and YEE, K.K., *Wear* (1966).
7. YAMANAKA, K. and ENOMOTO, Y., *J. Appl. Phys.,* **53,** 846 (1982).
8. MOORE, G.D. and RITTER, J.E., *J. Vac. Sci. Technol.,* **11(4),** 754 (1974).
9. YAMAGUCHI, T., HARANO, K.H. and YAJIMA, K., *Surface and Interfaces in Ceramic and Ceramic-Metal Systems,* J. Pask and A. Evans, eds., Plenum Press, NY, p. 503 (1980).
10. KLIMONDA, P., LINGSTUYL, O., LAVELLE, B. and DABOSI, F., *Surface and Interfaces in Ceramic and Ceramic-Metal Systems,* J. Pask and A. Evans, eds., Plenum Press, NY, p. 477 (1980).
11. BEINDT, C.C. and MCPHERSON, R., *Surface and Interfaces in Ceramic and Ceramic-Metal Systems,* J. Pask and A. Evans, eds., Plenum Press, NY, p. 619 (1980).
12. ELSSNER, G., DIEM, W. and WALLACE, J.S., *Surface and Interfaces in Ceramic and Ceramic-Metal Systems,* J. Pask and A. Evans, eds., Plenum Press, NY, p. 629 (1980).
13. CAMPBELL, D.S., *Mechanical Properties of Thin Films,* Handbook of Thin Film Technology, L.I. Maissel and R. Glang, eds., McGraw-Hill, NY (1970).
14. STECURA, S., *Am. Ceram. Soc. Bull.,* **56(12),** 1082 (1977).
15. MOTOJIMA, S., FUJIMOTO, A. and SUGIYAMA, K., *J. Mat. Sci. Letters,* **1,** 19 (1982).
16. PERUGINI, G., Proc. 3rd CIMTEC 3rd Intl. Meeting on Modern Ceramic Technologies, Rimini, p. 212, May (1976).
17. PERUGINI, G., GALANTE, F. and MARACCIOLI, E., Proc. 7th Intl. Metal Spraying conf., p. 143, London (1973).
18. BUNSHAH, R.F., *Evaporation,* CEI Course on Deposition Technol. and Their Applications, May (1981).
19. Conf. on Structure/Property Relationships in Thick Films and Bulk Coatings, *J. Vac. Sci. Technol.,* **11(4)** (1974).
20. BRISMAID, S., *et al.,* US Patent 2,784,115.
21. AUWARTER, M., US Patent 2,920,002.
22. BUNSHAH, R.F., *J. Vac. Sci. Technol.,* **11(4),** 814 (1974).
23. GRECO, V.P. and BALDAUF, W., *Plating,* **250,** March (1968).

24. BUNSHAH, R.F. and RAGHURAM, A.C., *J. Vac. Sci. Technol.*, **9**, 1385 (1972).
25. JACOBSON, B.E., *Microstructures of PVD-Deposited Films Characterized by Transmission Electron Microscopy*, Films and Coatings for Technology, Sweden (1981).
26. KOMIYA, S., UMEZU, N. and NARUSAWA, T., *Thin Solid Films*, **54**, 51 (1978).
27. ZEGA, B., KORNMANN, M. and AMIGUET, J., *Thin Solid Films*, **45**, 577 (1977).
28. SHERMAN, M., BUNSHAH, R.F. and BEALE, H.A., *J. Vac. Sci. Technol.*, **11**, 1128 (1974).
29. BOONE, D.H., STRANGMAN, T.E. and WILSON, L.W., *J. Vac. Sci. Technol.*, **11**, 641 (1974).
30. MOVCHAN, B.A. and DENUCHISHIN, A.V., *Fiz. Metall, Metalloved*, **28**, 653 (1969).
31. See ref. 34.
32. See ref. 40.
33. SCHINTLMEISTER, W., KAILER, K.H., WALLGRAM, W. and PACHER, O., *High Temp.-High Pr.*, **14**, 199 (1982).
34. THORNTON, J.A., *Plasmas in Deposition Process*, Deposition Technologies and Applications Course at Univ. California, June (1980).
35. COAD, J.P. and RESTALL, J.E., *Metal Technol.*, **9**, 499 (1982).
36. See ref. 34.
37. See ref. 34.
38. FRASER, D.B., *Thin Film Processes*, J.L. Vossen and W. Kern, eds., Acad. Press, NY, p. 131 (1978).
39. WAITS, R.K., *Thin Film Processes*, p. 131.
40. MATTOX, D.M., *Ion Plating Technology*, Films and Coatings for Technol. Vol. 1; B.E. Jacobson and R.F. Bunshah, eds.
41. TEER, D.G., *Evaporation and Sputter Techniques*, E. Lang, ed., Applied Sci., p. 79 (1983).
42. SHINNO, H., *et al.*, Proc. 7th ICVM Conf., Tokyo, p. 618 (1982).
43. OKAMOTO, I. and ARATA, Y., Proc. 7th ICVM Conf., Tokyo, p. 650 (1982).
44. MCCLANAHAN, E.D., Proc. 7th ICVM Conf., Tokyo, p. 481 (1982).
45. THORNTON, J.A., *Coating Deposition by Sputtering.*
46. CRAMER, S.D., *et al.*, *Electrodeposition of thick coatings of Pt and Pd on Refractory Metals for Aqueous Electrolytes*, US Dept. of Interior, Bur. of Mines, no. 7016, p. 158 (1967).
47. YEE, K.K., *Intl. Met. Rev.*, **23(1)**, 19 (1978).
48. BLOCHER, J.M., *J. Vac. Sci. Technol.*, **11(4)**, 680 (1974).
49. NEWHART, J.E., *Corrosion 73*, NACE, Houston, paper 113 (1973).
50, 51. STERN, K.H. and GADOMSKI, S.T., *J. Electrochem. Soc.*, **130**, 300 (1983).
52. GRECO, V.P. and BALDAUF, W., *Plating*, p. 250 (1968).
53. SAUTTER, F.K., *J. Electrochem. Soc.*, **110(6)**, 557 (1963).
54. PUSHPARAMAN, M., VARADARAJAN, G., KRISHNAMOORTHY, S., and SHENOI, B.A., *Electroplating and Metal Finishing*, p. 10, May (1974).
55. TUCKER, R.C., *Plasma and Detonation Gun Deposition Techniques and Coating Properties*, UCLA Course on Deposition Techniques and Applications, Sept. (1978).
56. KVERNES, I., *Coating of Diesel Engine Components*, E. Lang, ed., Applied Sci., p. 361 (1983).
57. MALIK, M.P., 7th Intl. Metal Spraying Conf., London, p. 257 (1973).
58. *Metallurgia*, **50(7)**, 299 (1983).
59. HOUBEN, J.M. and ZAAT, J.H., 7th Intl. Metal Spraying Conf., London, p. 11 (1973).
60. *Sprayed Unfused Metal Coatings for Engineering Purposes*, B.S. 4761, Brit. Std. Instn., London (1971).
61. *The Metallurgist and Materials Technologist*, p. 292, June (1975).
62. BENNETT, M.J., *et al.*, *Nucl. Technol.*, **66**, 518 (1984).
63. SMYTH, R.T., 7th Intl. Metal. Spraying Conf., London, p. 89 (1973).
64. KVERNES, I., *Coatings for High Temperature Applications*, E. Lang, ed., Appl. Sci., p. 361 (1983).
65. ARATA, Y., *et al.*, Proc. 7th ICVM Conf., Tokyo, p. 313 (1982, 1983).
66. YOSHIDA, T., TAKATA, R. and AKASHI, K., *Conf.*, p. 568.
67. MATSUMOTO, O., HAYAMI, E., KONUMA, M. and KANZAKI, Y., Proc. 7th ICVM Conf., p. 576, Tokyo (1982).
68. PRICE, M.O., WOLFLA, T.A. and TUCKER, R.C., *Thin Solid Films*, **45**, 309 (1977).
69. *Protective Coatings on Metals*, G.V. Samsonov, ed., Vol. 5, Consultants Bureau, NY (1973).
70. BENNETT, M.J., *Sol-gel and Vapour Deposition, Coatings for High Temperature Applications*, E. Lang, Appl. Sci., p. 169 (1983).
71. BENNETT, M.J., *J. Vac. Sci. Technol.*, **B12(4)**, 800 (1984).
72. GNANAMUTHU, D.S., *Applications of Lasers in Materials Processing*, E.A. Metzbower, ed., Proc. Conf. ASM, Washington DC, p. 177 (1979).
73. AYERS, J.D., *Lasers in Metallurgy*, Proc. Conf. Metall. Soc. AIME Chicago, Feb. 1981, K. Mukherjee and J. Mazumder, eds., p. 115 (1981).
74. WYNBLATT, P. and MCCUNE, R.C., *Surface and Interfaces in Ceramic and Ceramic-Metal Systems*, J. Pask and A. Evans, eds., Plenum Press, NY, p. 83 (1980).
75. BAILEY, E.P. and BORBIDGE, W.E., *Surface and Interfaces in Ceramic and Ceramic-Metal Systems*, J. Pask and A. Evans, eds., Plenum Press, NY, p. 525 (1980).
76. ALLEN, R.V. and BORBIDGE, W.E., *J. Mat. Sci.*, **18**, 2835 (1983).
77. PETTIT, F.S. and GOWARD, G.W., *Gas Turbine Applications, Coatings for High Temperature Applications*, E. Lang, ed., Appl. Sci. (1982).
78. KVERNES, I., *Coatings for High Temperature Applica-*

tions, E. Lang, ed., Applied Sci., NY, p. 361 (1983).

79. LOWELL, C.E., GRISAFFE, S.J. and LEVINE, S.R., NASA TM X–73499 (1976).
80. MILLER, R.A., *J. Am. Ceram. Soc.,* **67,** 517 (1984).
81. PETTIT, F.S. and GOWARD, G.W., *Coatings for High Temperature Applications,* E. Lang, ed., Applied Sci., NY, p. 341 (1983).
82. HINTERMANN, H.E., Proc. 8th Intl. Conf. on CVD, p. 473 (1981).
83. BERTINGER, R. and ZEILINGER, H., Proc. 8th Intl. Conf. on CVD, p. 664 (1981).
84. MOZAR, Th., FRANCKE, W. and TICHLER, J.W., Proc. 7th Intl. Metal Spraying Conf., London, p. 151 (1973).
85. MCCLANAHAN, E.D., BUSCH, R., FAIRBANKS, J. and PATTEN, J.W., ASME 74–GT–100 (1974).
86. MEHAN, R.L. and BOLON, R.B., *J. Mat. Sci.,* **14,** 2471 (1979).
87. AKIKAWA, N., UENUNA, T., MIKI, S. and MUTOH, M., Proc. 7th ICVM Conf., Tokyo, p. 330 (1982).
88. LAU, S.K. and BRATTON, R.J., *High Temperature Protective Coatings,* Proc. Symp. Atlanta, GA, March (1983), S.C. Singhal, ed., Metall. Soc. AIME, p. 305.
89. VENKATESH, V.C., *et al.,* Proc. 8th Intl. Conf. on CVD, p. 617 (1981).
90. CHO, J.S. and CHUN, J.S., Proc. 8th Intl. Conf. on CVD, p. 573 (1981).
91. RUPPERT, W., Proc. 8th Intl. Conf. on CVD, p. 489 (1981).
92. KVERNES, I., *Coatings for High Temperature Applications,* E. Lang, ed., Applied Sci., NY (1983).
93. KVERNES, I., 2nd Conf. on Advanced Materials for Alternative Fuel Capable Directly Fired Heat Engines, Monterey CA.
94. PERIGINI, G., GALANTE, F. and MARCACCIOLI, E., Proc. 7th Intl. Metal Spraying Conf., London. p. 143 (1973).
95. TUCKER, R.C., *Films and Coatings for Technology,* B.E. Jacobson and R.F. Bunshah, eds., Sweden, June (1981).
96. ZIRINSKY, S. and IRENE, E.A., *J. Electrochem. Soc.,* **125,** 305 (1978).
97. BENNETT, A., RESTALL, J.E. and SCOTT, K.T., private communication (1984).
98. DAHMAN, U., *et al., Surfaces and Interfaces of Ceramic and Ceramic-Metal Systems.,* Vol. 14, J. Pask and A. Evans, eds., Plenum Press, Metal Sci., p. 391 (1980).
99. TUCKER, R.C., *Films and Coatings for Technology,* B.E. Jacobson and R.F. Bunshah, eds., Sweden, June (1981).
100. TUCKER, R.C., *J. Vac. Sci. Technol.,* **11,** 725 (1974).
101. MATTING, H.A. and STEFFENS, H.D., *Metall.,* **17(6),** 583 (1983); **17(9),** 905 (1963).
102. VANVLACK, L.H., *The Metal-Ceramic Boundary,* Metals/Materials Congress, Philadelphia, PA, Tech. Report, p. (10-1-64) (1964).
103. GRISAFFE, S.J., NASA Tech. Note, NASA TN D–3113 (1965).
104. Union Carbide Corp., unpublished data.
105. MARCHANDISE, H., *The Plasma Torch and Its Applications,* European Atomic Energy Community, EUR 2439 f (1965).
106. LEVINSTEIN, M.A., EISENLOHR, A. and KRAMER, B.E., *Weld J., Weld Res. Suppl.,* **40,** 85 (1961).
107. WOLFLA, T.A., unpublished data.
108. LEEDS, D.H., *Some Observations on the Interface Between Plasma Sprayed Tungsten and 1020 Steel,* Defence Documentation Center, AD–803286 (1966).
109. BERNDT, C.C. and MCPHERSON, R., *Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems,* Vol. 14, J. Pask and A. Evans, eds., Plenum Press, Mat. Sci. Res., p. 619 (1980).
110. TEER, D.G., *Coatings for High Temperature Applications,* E. Lang, ed., Applied Sci., NY, p. 79 (1983).
111. BRYANT, W.A. and MEIER, G.H., *J. Vac. Sci. Technol.,* **11(4),** 719 (1974).
112. ZIRINSKY, S. and IRENE, E.A., *J. Electrochem. Soc.,* **125,** 305 (1978).
113. PERUGINI, G., GALANTE, F. and MARACCIOLI, E., Proc. 7th Intl. Metal Spraying Conf., London, p. 143 (1973).
114. MCPHERSON, R., *J. Mat. Sei.,* **15,** 3141 (1980).
115. KLIMONDA, P., LINGSTUYL, O., LAVELLE, B. and DABOSI, F., *Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems,* Mat. Sci. Res., Vol. 14, J. Pask and A. Evans, eds., Plenum Press, p. 477 (1980).
116. WHITTLE, D.P. and BOONE, D.H., Proc. 8th Internat. Congress on Metallic Corrosion, Mainz, p. 718, Sept. (1981).
117. DE-JIE, G., *et al.,* Proc. 7th ICVM Conf., Tokyo, p. 352 (1982).
118. CHILD, H.C., *Coatings for High Temperature Applications,* E. Lang, ed., Applied Sci., NY, p. 395 (1983).
119. PEPPER, S.V., NASA TM – 78838 (1978).
120. BRAINARD, W.A. and WHEELER, D.R., NASA TP 1377 (1979).
121. MATHEWS, A. and TEER, D.R., *Thin Solid Films,* **72,** 541 (1980).
122. ENOMOTO, Y., YAMANAKA, K. and MIZUHARA, K., Proc. 7th ICVM Conf., Tokyo, p. 209 (1982).
123. BHUSHAN, B., *Metal Finishing,* p. 71, June (1980).
124. KEDWARD, E.C. and WRIGHT, K.W., *Plating and Surface Finishing,* p. 38, August (1978).
125. CAMERON, B.P., FOSTER, J. and CAREW, J.A., *Trans. Inst. Metal Finishing,* **57,** 113 (1979).
126. NIIHARA, K. and HIRAI, T., Proc. 7th ICVM Conf., Tokyo, p. 180 (1982).
127. MOORE, G.D. and RITTER, J.E., *J. Vac. Sci. Technol.,* **11(4),** 754 (1974).
128. CLEGG, M.A., SILINS, V. and EVANS, D.J.I., Proc. 7th Intl. Metal Spraying Conf., London, p. 62 (1973).

129. HERMAN, H., *Ion Implantation into Metals,* V. Ashworth, W.A. Grant and R.P.M. Procter, eds., Pergamon Press, p. 102 (1982).
130. HALE, E.B., *et al., Ion Implantation into Metals,* V. Ashworth, W.A. Grant, R.P.M. Procter, eds., Pergamon Press, p. 111 (1982).
131. ZHONG-YIN, X., *et al, Ion Implantation into Metals,* V. Ashworth, W.A. Grant and R.P.M. Procter, eds., Pergamon Press, p. 117 (1982).
132. DELVES, B.G., *Ion Implantation into Metals,* V. Ashworth, W.A. Grant and R.P.M. Procter, eds., Pergamon Press, p. 126 (1982).
133. ROBERTS, S.G. and PAGE, T.F., *Ion Implantation into Metals,* V. Ashworth, W.A. Grant and R.P.M. Procter, eds., Pergamon Press, p. 135 (1982).
134. DEARNLEY, G., *Ion Implantation into Metals,* V. Ashworth, W.A. Grant and R.P.M. Procter, eds., Pergamon Press, p. 180 (1982).
135. TUCKER, R.C., *J. Vac. Sci. Technol.,* **11(4)**, 725 (1974).
136. BARNHART, R.E., "The Contribution of Metallic and Ceramic Coatings to Gas Turbine Engines", contributed by the Gas Turbine Div., ASME, Gas Turbine Conf. and Products Show, Washington DC (1968).
137. HURRICKS, P.L., *Wear,* **22**, 291 (1972).
138. DONOVAN, M. and SANDERS, J.L., *Tribology,* **5**, 205 (1972).
139. GERDEMAN, D.A. and HECHT, N.L., *Arc Plasma Technology in Materials Science,* Springer-Verlag, NY (1972).
140. *Coatings for High Temperature Applications,* E. Lang, ed., Applied Sci., NY (1983).
141. *High Temperature Oxidation Resistant Coatings,* Natl. Acad. Sci., Washington DC (1970).
142. Patent counsel, Marshall Space Flight Center, Alabama USA, Orders to Tech. Alert, Room 206, Ebury Bridge House, Ebury Bridge Road, London SW1W 8QD.
143. STEFFENS, H.D. and CROSTACK, H.A., 9th Intl. Thermal Spraying Conf., The Hague, p. 120, May (1980).
144. NICOLL, A.R., *Coatings for High Temperature Applications,* E. Lang, ed., Applied Sci., NY, p. 269 (1983).
145. YAMANAKA, K. and ENOMOTO, Y., Proc. 7th ICVM Conf., Tokyo, p. 157 (1982).
146. YAMANAKA, K. and INOMOTO, Y., *J. Appl. Phy.,* **53**, 846 (1982).
147. CROSTACK, H.A. and STEFFENS, H.D., *Behaviour of Joints in High Temperature Materials,* T.G. Gooch, R. Hurst, H. Kroeckel and M. Merz, eds., Applied Sci., p. 217.
148. STEFFENS, H.D. and CROSTACK, H.A., Proc. 7th ICVM Conf., Tokyo, p. 360 (1982).
149. SCHMITZ, V., Fh.G. Berichte 1 (1977).
150. STEFFENS, H.D. and CROSTACK, H.A., Proc. Internat. Conf. on Metallurgical Coatings, Am. Vac. Soc. (1981).
151. GREEN, D.R., *Nucl. Sci. and Eng.,* **12**, 271 (1962).
152. CROWE, J.C. and DAWSON, J.F., *Applications of Infrared NDT Techniques to Hardface Coating Bond Inspection,* BNWL-B-427 (1975).
153. SCOTT, G.W., *et al., Nondestructive Inspection of Thin Plasma-Sprayed Ceramic and Cement Protective Coatings for Coal Conversion and Utilization Equipment,* ORNL/TM-6210 (1968).
154. GREEN, D.R. and DAY, C.K., ASTM Special Tech. Pub. No. 439, ASTM, p. 4 (1968).
155. GREEN, D.R., *J. Appl. Optics,* **7**, 1779 (1968).
156. GREEN, D.R., SCHMELLER, M.D. and SULIT, R.A., *Oceans 82,* IEEE.
157. GREEN, D.R., *J. Appl. Phys.,* **37**, 3095 (1966).
158. GREEN, D.R., *Materials Evaluation,* **25**, 231 (1969).
159. GREEN, D.R., *et al., Thermal Spray Testing,* CME 126, Tech. Alert Room 373, Ashdown House, 123 Victoria St., London, SW1E 6RB.
160. STANTON, W.E., Proc. 7th Intl. Metal Spraying Conf., London, p. 157 (1973).
161. BOURGOIN, P.B., Proc. 7th Intl. Metal Spraying Conf., London, p. 185 (1973).
162. HANSMAN and MOSLE, *Adhesion,* **26**, 18 (1982).
163. HANSMAN and MOSLE, *Adhesion,* **25**, 332 (1981).
164. SOLOMIR, J.G., Proc. 7th Intl. Metal Spraying Conf., London, p. 194 (1973).
165. KOHNO, M. and KUWAHARA, K., Proc. 7th ICVM Conf., Tokyo, p. 216 (1982).
166. KEDWARD, E.C., ADDISON, C.A. and TENNETT, A.A.B., *Trans. Inst. Metal Finishing,* **54** (1976).
167. KEAR, B.H. and THOMPSON, E.R., *Science,* **208**, 848 (1980).
168. FOROULIS, Z.A. and PETTIT, F.S., eds., *Proc. Symp. Prop. High Temp. Alloys With Emphasis on Environmental Effects,* Electrochem. Soc., Princeton NJ (1976).
169. CLEGG, M.A., SILINS, V. and EVANS, D.J.I., Proc. 7th Intl. Metal Spraying Conf., London, p. 62 (1973).
170. KAMO, R., *et al.,* Proc. Conf. on Advanced Materials Maine, for Alternative Fuel Capable Directly Fired Heat Engines, Maine, p. 832, Dec. (1979).
171. KAMO, R., *et al.,* Proc. Conf. on Advanced Materials Maine, for Alternative Fuel Capable Directly Fired Heat Engines, Maine, p. 832, Dec. (1979).
172. SLINEY, H.E., NASA TM 79113 (1979).
173. KVERNES, I., SOLBERG, J.K. and LILLERUD, K.P., Proc. Conf. on Advanced Materials, Maine, for Alternative Fuel Capable Directly Fired Heat Engines, Maine, p. 233, Dec. (1979).
174. PERUGINI, G., Proc. 3rd CIMTEC 3rd Internat. Meeting on Modern Ceramic Technologies, Rimini, p. 212, May (1976).
175. HOUBEN, J.M. and ZAAT, J.H., Proc. 7th Intl. Metal Spraying Conf., London, p. 77 (1973).
176. SOLOMIR, J.G., Proc. 7th Intl. Metal Spraying Conf., London, p. 194 (1973).
177. KVERNES, I., *Coatings for High Temperature Applications,* E. Lang, ed., Applied Sci., NY, p. 361 (1983).
178. *Coatings for High Temperature Applications,* E. Lang, ed., Applied Sci., NY (1983).