

THERMALLY SPRAYED COATINGS: PROPERTIES AND APPLICATIONS

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ABSTRACT

Thermally sprayed coatings are produced from the repeated deposition of particles that are in the diameter range of 10 to 120 microns. The coating structure may be described as being of lamellar morphology. These coatings are used in high temperature, corrosion, tribological and component reclamation applications. This paper relates the material properties of coatings to their service performance. It is intended to establish criteria whereby the unique characteristics of thermally sprayed materials can be used to advantage.

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INTRODUCTION

Thermal spray technology has distinctive processing attributes; such as the ability to coat most materials with an almost unlimited range of ceramics. It is also possible to produce thick coatings from 0.1 to 2 mm routinely and to control the precise coating formulation and chemistry for a specific application.

The principal professional groups who have an interest in thermal spray technology are listed in Fig. 1. The topics of interest often overlap for these groups. For instance, it is difficult to distinguish between the experience (or "art") of a thermal spraying contractor and the well-defined procedures that an engineer must develop.

The major forum for thermal sprayers and technologists to meet since 1956 has been at the International Thermal Spray Conferences (1-4). The first seven of these meetings up to 1973 were known as International Metal Spraying Conferences. Since the mid-80's several other meetings have been convened. These are the National Thermal Spraying Conferences (organized by ASM International) (5,6), the Plasma-Technik meeting (7) (a Swiss company) and the Advanced Thermal Spraying and Allied Coatings Symposium (8) (organized by the High Temperature Society of Japan). Several books (9,10) and reviews (11-13) have also summarized the literature.

The different disciplines encompassed by thermal spraying				
		SCIENCE	ENGINEERING	PRACTICE
The division of thermal spraying into different topics	The Process	<ul style="list-style-type: none"> ● Plasma arc physics ● Combustion ● Diagnostics 	Design and manufacture of <ul style="list-style-type: none"> ● Torches ● Equipment 	<ul style="list-style-type: none"> ● Process control
	Micro-Structure	<ul style="list-style-type: none"> ● Characterization of Chemistry, Porosity, Phases etc ● Modelling of process 	<ul style="list-style-type: none"> ● The need for quality control ● Residual stress considerations ● Powder production 	<ul style="list-style-type: none"> ● Thermal spraying tables
	Testing and Properties of Coatings	<ul style="list-style-type: none"> a Mechanical properties ● Thermal properties ● Corrosion behaviour ● Electrical properties 	<ul style="list-style-type: none"> ● Mechanisms ● Modelling ● Prediction 	<ul style="list-style-type: none"> ● Suitability of coating ● Interface with consumers
	Applications	<ul style="list-style-type: none"> ● Interface with consumers, engineers and contractors ● Plan future applications 	<ul style="list-style-type: none"> ● Solve and advise on specific problems /applications a Design coating 	

Figure 1. Thermal spray interest groups and areas of expertise.

STRUCTURE AND PROPERTIES OF COATINGS

Thermally sprayed coatings have a lamellar microstructure (14). The layered structure forms due to the repeated deposition of molten and semi-molten particles. Porosity and microcracks can be distinguished within single splats. Figure 2 illustrates the features of a well-melted powder that has formed a coating. The resultant lamellar dimensions are about 60 microns in diameter and from 1 to 2.5 microns thick (15). Every coating structure is highly oriented with the lamellae parallel to the surface of the substrate.



Figure 2. Surface features of a well-melted ceramic coating.

It has been estimated (15) that the real contact area of lamellae with the substrate and within the coating is 30% of the available boundary area. Direct measurements (16) of the **interlamellar** porosity have shown that the porosity is about 10 to 100 nm in size. Unmolten particles become incorporated into the coating and these, along with the interlamellar boundaries and porosity, constitute regions of poor bonding which may lead to failure of the coating system. In cross-section the structure is layered, Fig. 3.

Thermally sprayed ceramic coatings are used with a 0.1-0.2 mm thick metallic layer which is applied to the substrate prior to the ceramic coating. Such layers (17,18) improve the bonding property of the ceramic layer which is deposited and the term "**bond coat**" is used. Bond coatings are based on alloys of nickel, chromium, molybdenum and aluminium; with some additions of yttrium in special cases. Most ceramic coatings include a bond

coat. This bond coat can be considered as a compliant layer that compensates for stresses which may arise from the ceramic overlay. A model for the coating profile is presented in Fig. 4.

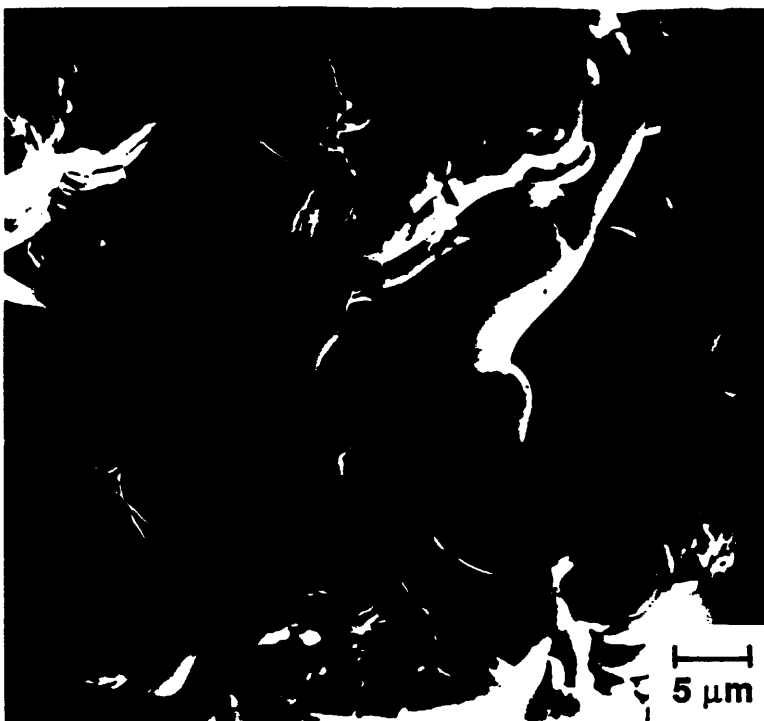


Figure 3. Cross-section of a fractured thermally sprayed coating.

SCHMATIC OF A OUPLM COATING STRUCTURE

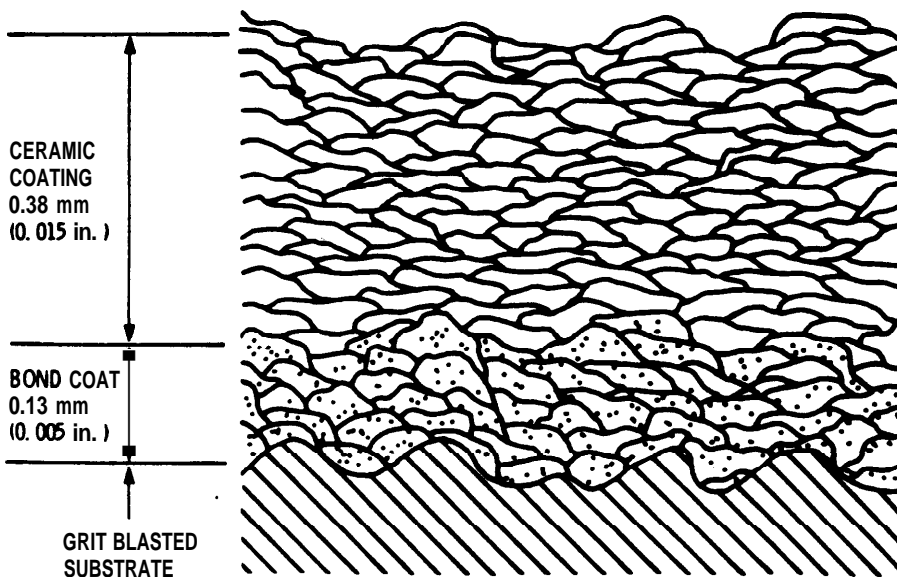


Figure 4. Sketch of coating cross-section.

The material **properties** of coatings are a direct consequence of their complex structure; and this, in turn, determines the overall coating behaviour (19-21). Not all coatings are used in their as-sprayed condition. Coatings which are used in wet environments (such as for pump sleeves or bearings) may be filled with an epoxy prior to machining and polishing. The additional epoxy treatment fills any surface porosity that may have allowed environmental ingress and thereby have expedited the breakdown of the coating. Other post-processing surface treatments such as laser-glazing (22-24) and hot isostatic pressing (25) have been used to densify coatings.

Coatings are suited to specific applications because they retain some intrinsic material characteristic of the original coating powder. However it must be emphasized that "bulk" ceramic performance can not be directly correlated to any property of the coating. The structure of a coating is quite dissimilar to that of a material produced by a bulk fabrication process. The material properties of the **coating** that may limit its utility include the mechanical, thermal and electrical properties. An additional property of great interest is adhesion to the substrate (26,27) since it is crucial for the coating to remain attached throughout its intended service life.

Table 1 lists thermal spray processes (28,29). Those which are based on similar technological principles or which have equivalent names are grouped onto separate lines. The choice of process or material depends on the engineering application. Ceramics generally require processes with higher velocities and temperatures than low melting point materials. Therefore, plasma, D-gun and HVOF are the preferred techniques for deposition at high rates. The deposition of ceramics is more sensitive to spray parameters than is the deposition of metals.

Table 1. Thermal spray processes.

1. Oxy-acetylene gas flame spraying, flame spraying
2. Atmospheric plasma spraying, APS
3. Low pressure plasma spraying, LPPS, VPS
4. Detonation gun spraying, D-gun
5. Ceramic rod process, Rokide process
6. Fuel air repetitive explosion process, FARE gun
7. Hypersonic plasma spraying, diamond jet gun (DJ gun), Jet Kote, High velocity oxy-fuel process (HVOF), J-gun, Topgun, Nova-jet, Plazjet
8. Arc metallization
9. Wire spraying
10. Wire explosion process

CLASSIFICATION OF APPLICATIONS

Table 2 presents the range of applications that may take advantage of thermal spray technology. Major usage

areas for coatings . are component reclamation and corrosion control. The coating structure and character are a complex relationship between powder variables (Eg, particle size, morphology and chemistry) and thermal spray parameters. Figure 5 (adapted from reference 30) summarizes some of the interdependencies between these variables.

Table 3 shows the range of industries that use thermal spray technology. Some of these industries rely on the thermal spray process for primary processing; for example to manufacture powders; whereas others use coatings in a secondary industry either as a commodity material or for an engineering application.

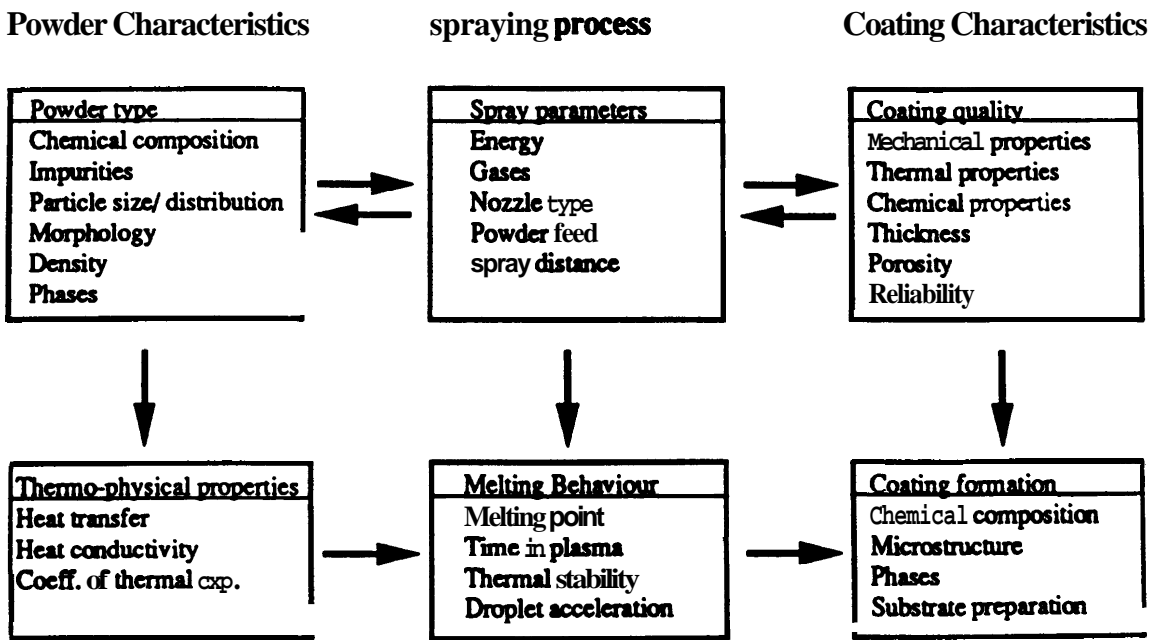


Figure 5. Variables during thermal spraying processes.

Table 2. Applications of thermal spray coatings.

1. Rebuilding and salvaging worn components
2. Electronic materials, insulating surfaces, dielectrics
3. Thermal barriers and thermal insulation materials
4. Bioceramic materials
5. Hard and wear resistant materials
6. Hot corrosion control
7. Wet corrosion control
8. Superconducting materials
9. Solid lubricant materials
10. Cavitation control
11. Near-net shape processing, manufacture of composites
12. Abradable and abrasive materials for sealing applications
13. Plasma processing of materials
14. Magnetic shielding, radio-frequency shielding

Table 3. Industries that use thermally sprayed materials.

1. Aerospace industry
2. Automotive industry
3. The military sector
4. Biomedical industry
5. Powder production
6. Steel making industry
7. Off-shore engineering
8. Nuclear and power generation industry
9. Heavy industries (papermaking, mining, textile, printing)
10. Engineering maintenance

APPLICATIONS FOR CERAMIC COATINGS

Not all coating applications will be covered. Table 4 lists specific uses of coatings. Several applications will be described in which these coatings are preferred to other engineering solutions.

Turbine applications

Thermal barrier coatings (TBCs) consist of alloys of zirconia with stabilising oxides such as yttria, magnesia, calcia or ceria (31-39). These coatings are used on the compressor, combustion chamber, fuel vaporisers, nozzle guide vane platforms and turbine aerofoil components of aero-engines. The coatings are, for example, deposited to 0.38 mm thickness over the airfoil surface of turbine blades.

Coatings which are based on WC-Co powder composites are applied to the compressor fan and disc mid-span stiffeners to prevent wear; and to the compressor airfoils to control particulate **erosion** (40). These coatings are formed from cermet composite powders that may be produced by a **micro-pelletization** process.

Some aero-engine parts require good sealing between the rotating and stationary components to maintain high compression of gases. In these applications an abradable coating is formed on the stationary component, such as the compressor, and an abrasive material may be coated onto the tip of the turbine blade or onto the disc spacer, (40,41). Thus the turbine will maintain the minimum clearance between the rotating components and thereby achieve optimum engine efficiency. The abradable coatings are manufactured as composites of graphite with either nickel or aluminium; or they may consist of nichrome with a polyester or polyurethane. Figure 6 (40) illustrates two applications of abradable and abrasive coatings to seal airfoil systems which have rotating components. The coating system may be **multi-layered** and Fig. 7 shows an example where a combination of 4 coatings provide a thermal barrier and an abradable coating (40).

Table 4. Applications of thermally sprayed coatings.

Hard surfaces	<ul style="list-style-type: none"> - sizing punches, extrusion dies - pump seals - hot crushing rolls - hot forming guides
Control of abrasive rain wear	<ul style="list-style-type: none"> - buffing and polishing machines - polishing rod liners
Adhesive wear	<ul style="list-style-type: none"> - piston guides - thrust bearing shoes - bronze and babbitt bearings
Hard bearings	<ul style="list-style-type: none"> - fuel pump rotors - impeller shafts - piston rings - armature shaft journals
Fretting	<ul style="list-style-type: none"> - cylinder liners - automotive valves - rocker arms - lathe and grinder dead centres
Cavitation	<ul style="list-style-type: none"> - water turbine buckets - wear rings in hydraulic turbines - impeller pump housings
Particle erosion	<ul style="list-style-type: none"> - exhaust fans - cyclone dust collectors - exhaust valve seats
Heat and oxidation resistance	<ul style="list-style-type: none"> - tuyeres for liquid metal - continuous casting moulds - heat treating fixtures and brazing jigs - exhaust mufflers
Atmospheric and immersion corrosion	<ul style="list-style-type: none"> - electrical conduits - bridges - transformer cases - steam cleaning equipment - ship superstructures - ship holds and tanks - storage tanks for oils, fuels and solvents - power line hardware - heat exchangers
Electrical conductivity and resistivity	<ul style="list-style-type: none"> - ground conductors - lighting arrester - ground cating for locomotive axles
Machine element clearance control	<ul style="list-style-type: none"> - air seals (to replace silver) - aircraft engine components - compressor seals (to replace rubber)

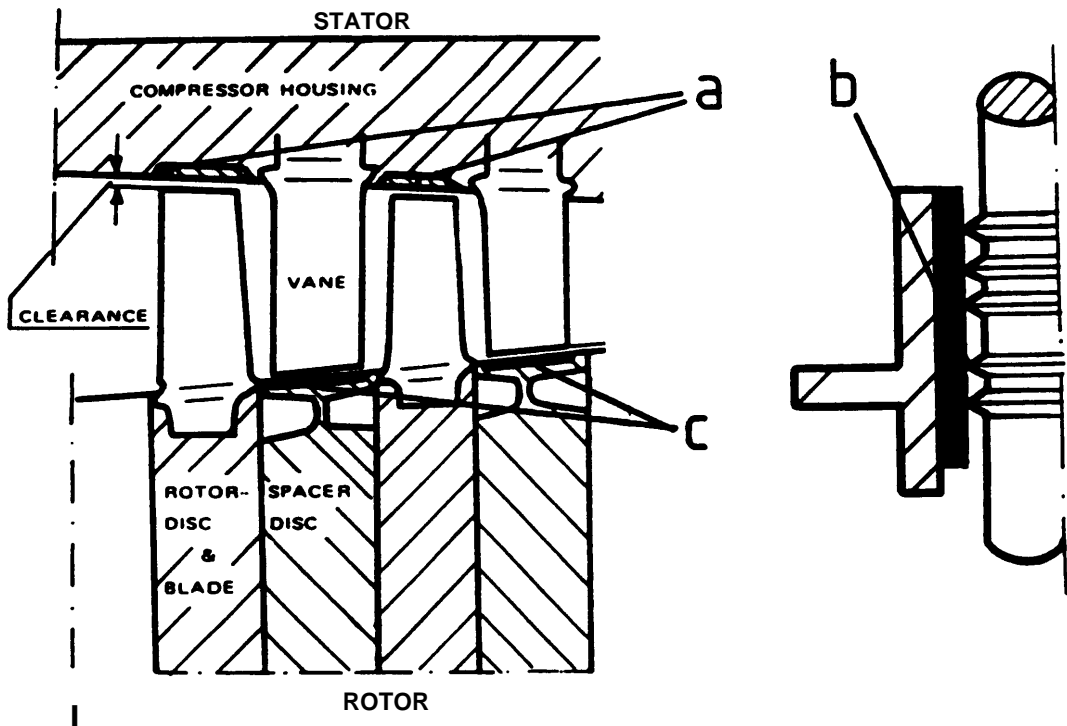


Figure 6. Sealing applications for thermally sprayed coatings. The two sketches show the use of abradable coatings on (a) compressor housings and (b) labyrinth fins; and abrasive coatings on (c) disc spacers (adapted from reference 40).

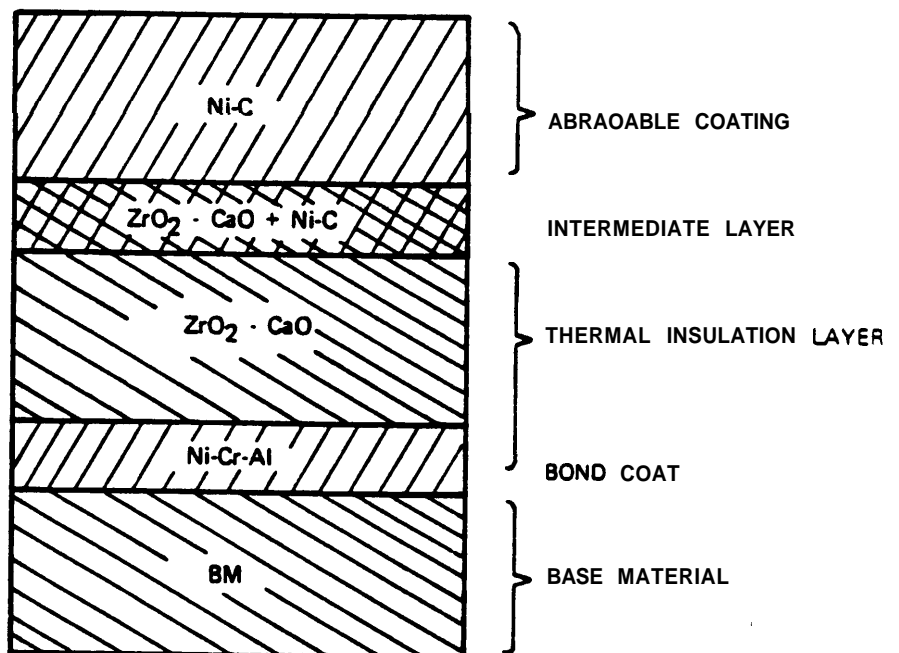


Figure 7. Coating system for a thermal barrier and abradable coating (from reference 40).

Diesel engine applications •

Thermal barrier coatings have also been used in diesel engines (42-46). The zirconia-yttria alloy coatings may improve fuel efficiency by insulating the combustion chamber area of the engine, thereby recovering the 8 to 15% of the energy that is attributed to heat losses. The coatings have been applied to the cylinder head, the valves, the piston, and the liner top (to 1.5 mm thickness), Fig. 8. A molybdenum coating can be applied to piston rings to ensure long term sealing of the combustion chamber. Figure 9 shows the thickness variation in the bowl area of a piston crown which has been coated with a zirconia ceramic alloy (43).

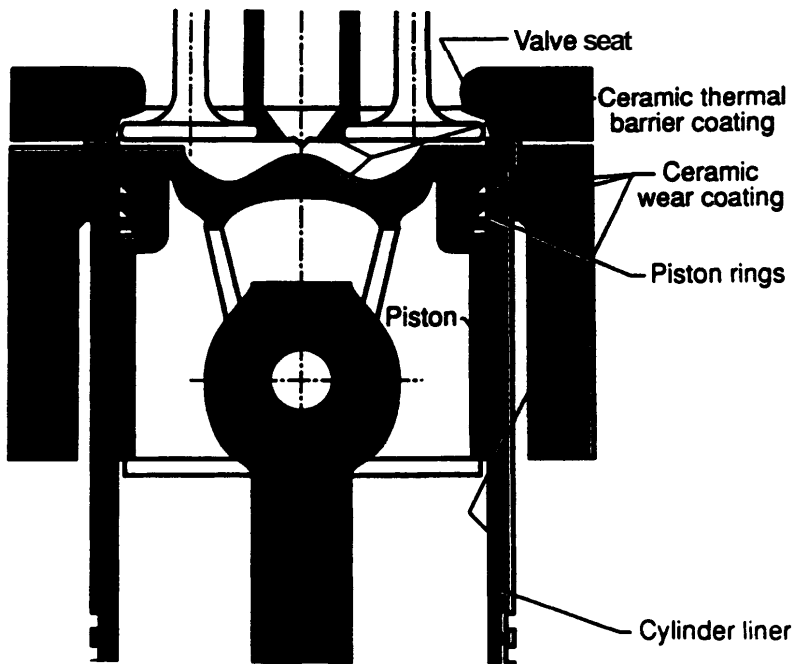


Figure 8. Ceramic usage within automobile engines (after reference 46).

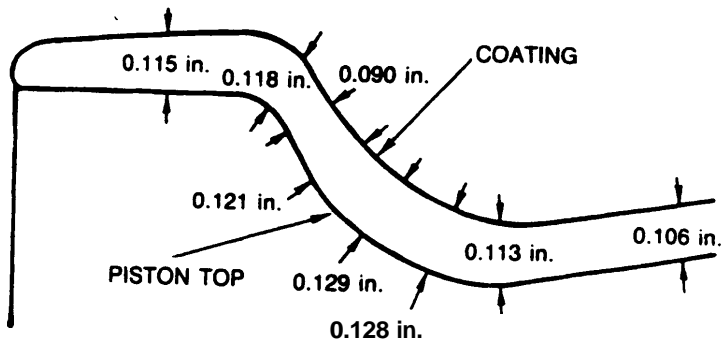


Figure 9. Coating thickness variation of zirconia ceramic on piston crown (43).

Bioceramic coatings

Coatings based on the apatite system have been used to improve the fixation of prosthetic appliances to the human anatomy (47-51). This work has evolved from the pioneering research of Brown et al. (52-56). Ceramics such as hydroxyapatite can be thermal spray deposited onto the stems of artificial hips and then the engineering assembly directly inserted into the prepared femoral bone. The prime advantage is that it is not necessary to use an epoxy to glue the prosthesis into place. It has been established that epoxy leads to necrosis of the immediately surrounding bone tissue and this may cause loosening of the prosthesis (and pain) over the lifetime of recipient. On the other hand the porous nature of the hydroxyapatite coating allows the natural bone to grow into the bioceramic coating. It is postulated that the hydroxyapatite coating is gradually resorbed and this change in ceramic function is progressively accommodated by new bone formation, Fig. 10.

This bioceramic application relies on two material properties which are usually thought to limit the component life; these are the porosity and environmental degradation. Thus a major design requirement is to manufacture a coating with a specific porosity size and distribution (49,58). The coating must also be gradually resorbed into the body so that natural osteo-integration can proceed.

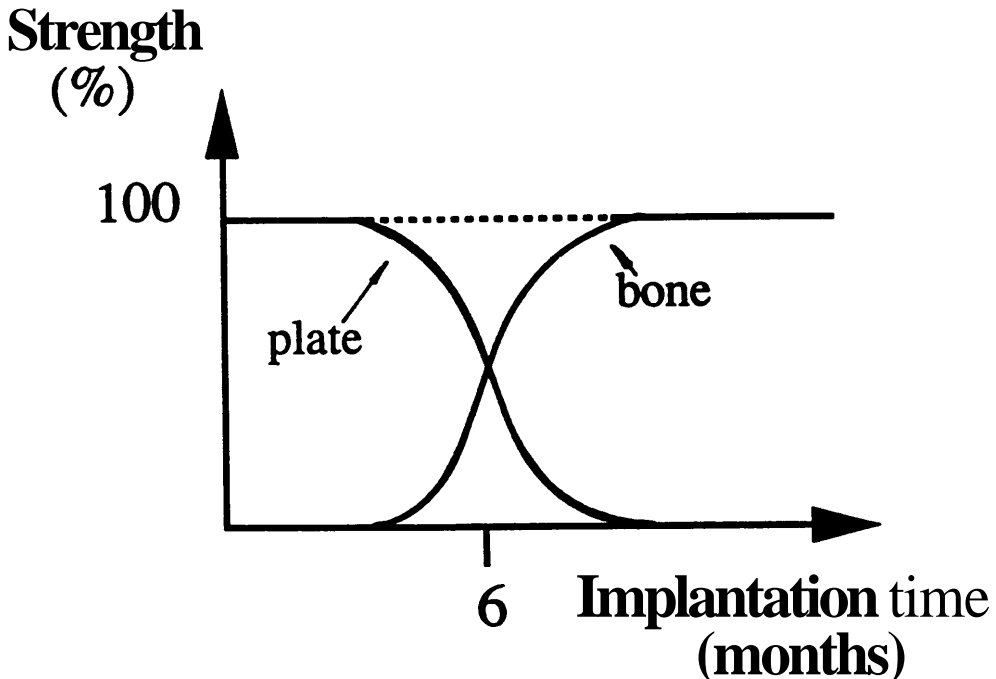


Figure 10. Strength vs. time behaviour of bone and re-sorbable ceramic (adapted from reference 57).

Heavy industry applications

The most commonly used coatings are based on alumina. For example alumina, **alumina-zirconia** composites, alumina-magnesia (spinel), alumina-silica (mullite) and magnesium zirconate (MgZrO_3) have been used (59) as 1 mm thick coatings to prevent slag attack on the refractory linings of slide gate plates, stoppers, tundish nozzles and crucibles in the steel making industry. It is a prime requirement for the coating to have low porosity so that the slag has a minimum surface area over which to react. Other important specifications are related to a high bond strength of the coating, good wear characteristics and the ability to resist thermal shock. The requirement for a high bond strength is not considered essential for the coating to perform satisfactorily since materials with strengths of 5 MPa are quite successful.

Alumina, **alumina-titania** and **alumina-nichrome** materials have been used (60) to form coatings that extend the life of hot extrusion dies. The coatings prevent heat loss through the die during the extrusion process and control wear of the die material. Die life increases by a factor of 7 and improved productivity (it is claimed) by 100% since production runs are no longer halted by frequent die changes. The product quality was also improved since the tolerances and surface finish of the product are maintained for longer periods.

Rolls are used throughout heavy industries to transport material; for example in a steel plant, or to shape and process materials such as in the textile, chemical and printing industries. The thermal spraying of WC-Co materials by high velocity processes such as D-gun (61,62) and Jet Kote has found increasing use since the late 1970's. The coatings protect gate valves, seal surfaces, compressor rods, wire drawing capstans and die profiles.

Plasma spraying of alumina-zirconia composite material has been applied to the cooling rolls in continuous annealing lines. (63). These coatings successfully replaced electroplated chromium and they were **superior** to thermally sprayed carbide coatings. It was established that 0.2 mm thick coatings exhibited an appropriate heat transfer coefficient. This allowed uniform cooling of the sheet steel product and the coatings were reliable in terms of good wear and thermal shock resistance.

Blast furnace tuyeres operate under an extremely demanding environment and have a limited life due to thermal overloading, mechanical abrasion, manufacturing defects, and hot slag and liquid metal attack. Their life has been extended (64) by the application of a three layer system of metal-ceramic composite materials. The initial layer is applied directly to the copper tuyere by

pack diffusion of aluminium. Then two layers are thermally sprayed and consist of (i) 65wt% NiCrAl (of composition 74:20:6, respectively) - 35wt% magnesium zirconate; and then, (ii) a ceramic-ceramic composite of 75wt% zirconia and 25wt% magnesia.

Alumina and rutile have been plasma sprayed onto glass coated steel tanks to repair defects in the sodium-silicate lining (65). These tanks are used to prevent corrosion in the chemical industry and the reclamation of the tank represents a major economic and productivity gain. The major factor in the preparation of these coatings was to keep the surface temperature of the substrate (ie, the silicate glass) between 500 to 600°C. This thermal spraying parameter was controlled by the powder feed rate and the spraying distance. The tensile strength of the repair coating at higher substrate temperatures was unacceptable due to thermal shock cracking of the silicate substrate. No bond coat procedures were necessary to obtain coatings 0.3 mm thick,

Power generation plant applications

The flame, plasma and arc metallization processes are well suited for the spraying of metal layers which combat high temperature corrosion in power generation plant applications (66-68). Ceramics and cermets are also sprayed by the D-gun process (69). The best coating was a composite of chromium carbide and nichrome applied 0.3 mm thick. This composite coating behaved more favourably than coatings of alumina, zirconia and tungsten carbide-cobalt under service conditions which control erosion due to fly ash.

Electrical industry applications

Electrically insulating coatings have been fabricated out of alumina (70,71), spinel, cordierite and forsterite (71). Coatings of silicon have been sprayed for the manufacture of solar cells (72,73) and resistors, which are based on NiO-Fe₃O₄ mixtures, have also been satisfactorily thermally sprayed and tested (74).

Electrically conductive coatings resistant to wear (75) have been manufactured from titanium diboride in an aluminium bronze matrix and zirconium carbide in aluminium bronze matrix. Zirconium carbide in copper base composite also demonstrated good conductivity.

CONCLUDING REMARKS

The applications of thermal spray technology are varied. Thermal spray coatings are sometimes disadvantaged as a process since they are formed by a line-of-sight process and therefore components may not be suitably shaped for uniform coating deposition. For example Fig. 9 reflects this drawback since coatings for

piston crowns are of variable thickness and this may not suit the application. In some instances the thermal spray coating can be applied in the field without removal to a specialized reclamation facility. It is now standard procedure for coatings to be applied in the original equipment manufacture resulting in significant economic gain.

It is difficult to separate metal and ceramic applications for thermally sprayed coatings since these materials are often used together. The metal may act as a bond coat to improve adhesion or the metal can be co-sprayed with the ceramic to form a cermet composite. The powders may be premixed in a mechanical fashion or a composite powder can be manufactured which has the different components bound together in each particle. The two powders may also be feed to the thermal spraying torch by two different delivery systems.

Areas that have not been covered in this article include the manufacture of near-net shapes, composite technology and superconductors. In some cases the applications are well-established (76); for instance in the manufacture of free standing alumina radomes. However the long term utility of this technology relies on the development of more advanced manufacturing processes which involve composite technology. This includes the co-deposition of continuous (77,78) and discontinuous (79) fibres into a thermally sprayed matrix. The research area of high temperature superconductors (80-82) is also not covered since it has not, to date, shown a commercial advantage over other processes. The **prime** shortcoming of the thermal spray route is that the so-formed coatings exhibit low critical current densities that are not competitive with thin film technology.

The coating microstructure and phase distribution of thermally sprayed coatings are dissimilar to those of the bulk constituents. Therefore material properties of the coating; such as thermal diffusivity, mechanical strength in tension and shear, and wear characteristics will be different from the properties of the bulk material. Thus the microstructure of coatings determine their utility and this recognition enables the user to take full advantage of coating properties.

ACKNOWLEDGEMENTS

This work has been supported by many funds which include the Ian Potter Foundation, the Faculty of Engineering (Monash) and the Monash Research Fund. The work was initially presented at the 7th CIMTEC (World Ceramics Congress), Italy, 1990.

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