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MECHANICAL, THERMOMECHANICAL AND TRIBOLOGICAL APPLICATIONS OF CERAMIC COATINGS

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This paper will focus on ceramic coatings which are manufactured by thermal spraying. This 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 on a routine basis and the precise coating formulation and chemistry may be controlled for a specific application. It is intended to give examples where thermal spray coatings can, and indicate where they can not, find utility; and in this fashion a basis on their application will be adjudged.

1. INTRODUCTION

Thermal spray technology has been used to solve problems of an engineering nature since the late 1940's. The **principle** professional groups who have an interest in this technology are listed in Table 1. The topics of interest which are indicated will overlap in both the theme and the discipline categories. For instance, it is sometimes difficult to distinguish between the experience (or "**art**") of a thermal spraying contractor and the well-defined procedures that an engineer must develop. The outcome of both groups is exactly the same; ie, high-quality coatings, however the methods by which this is achieved may be quite divergent. A hierarchy of connections does exist between the various interest groups and this network relies on the assumption that basic or applied knowledge can be transferred into a marketing commodity.

The literature on thermal spraying is divided between scientists and practitioners. The major forum for these groups to meet since 1956 has been at the International Thermal Spray Conferences (ITSC). The first 7 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), the Plasma-Technik meeting (a Swiss company) and the Advanced Thermal Spraying and Allied Coatings Symposia (organized by the High Temperature Society of Japan). The International Conference on Metallurgical Coatings

TABLE 1. PRINCIPLE INTEREST GROUPS IN THERMAL SPRAY TECHNOLOGY

		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"> ● thermal spraying tables
	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 	
	Testing and Properties of Coatings	<ul style="list-style-type: none"> ● 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 ● design coating 	

and the American Ceramics Society Meeting usually have at least one session devoted to the thermal spraying of materials.

The present work will report on some of applications that have been presented at thermal spray meetings over the most recent **15¹⁻⁸** years. The definition of "ceramic" will be taken in its most broad context and may include classical ceramics such as alumina; high-tech materials such as **zirconia** alloys; and the refractory materials based on carbides.

2. THE STRUCTURE AND PROPERTIES OF COATINGS

Thermally sprayed coatings have a microstructure that is often described as being of lamellar morphology⁹. The structure is formed from the repeated deposition of molten and semi-molten particles. The resultant lamellar dimensions are about 60 microns in diameter and from 1 to 2.5 microns **thick**¹⁰; and it can be noted that every coating structure is highly oriented with the lamellae parallel to the surface of the substrate. It has been **estimated**¹⁰ that the real contact area of lamellae is 30% of the available boundary area and direct **measurements**¹¹ of the porosity have shown that the interlamellar porosity is about 10 to 100 nm in size. Unmolten particles may become incorporated into

the coating and these, along with the interlamellar boundaries and porosity, constitute regions of poor bonding which ultimately may lead to failure of the coating system.

Thermally sprayed ceramic coatings are rarely used alone and it is common practice to incorporate a 0.13 mm metallic layer onto the substrate. Such layers improve the bonding action of the ceramic layer which is deposited; and therefore these layers are referred to as "bond coats". These coatings are based on alloys of nickel, chromium, molybdenum and aluminium; with some additions of yttrium in special cases. Thus, although the topic of the present work is focussed on ceramics, it is usually assumed that the entire coating system consists of a bond coat with a ceramic overlay.

The quite complex structure of coatings has important implications with regard to its service performance since this structure ultimately determines the overall coating behaviour. It can also be pointed out that not all coatings are used in their as-sprayed condition. Coatings which are used in a wet environment (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**¹² and hot isostatic **pressing**¹³ have also been used to densify the coating.

The coating applications are a direct consequence of their ability to retain some **intrinsic** ceramic characteristics; 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 which is 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 the adhesion property of the coating to the substrate^{14,15} since it is crucial for the coating to remain attached throughout its service life.

3. CLASSIFICATION OF APPLICATIONS

Table 2 presents the broad range of applications that may take advantage of thermal spray technology. It can also be noted that several thermal spraying technologies, such as plasma, flame, Jet Kote, arc metallization and **D-gun**¹⁶ are available. Reference will only be made to a particular process if the specific application or material is process dependent. It is generally observed that the higher temperature plasma processes are more frequently used for ceramic materials.

Table 3 shows the range of industries that presently take advantage of thermal spray coatings. Some of these industries rely on the thermal spray process as a primary resource; for example to manufacture powders or control toxic wastes; whereas others use coatings in a secondary industry either as a commodity material or for an engineering

TABLE 2. THE APPLICATIONS SPECTRUM 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

application. Polymer industries are not well represented as users of thermal spray coatings.

Not all of the applications shown in Table 2 are referenced with respect to ceramic coatings; for example the off-shore industry uses the thermal spraying of metal to combat **corrosion**; and many engineering workshops use metal coatings to reclaim worn components. The present focus will be on ceramics and **specific** applications are detailed below.

4. APPLICATIONS FOR CERAMIC COATINGS

Not every application that is used for ceramic coatings will be covered; since such data is readily available from the many companies, consultants and contractors who specialize in thermal spraying processes. However several applications will be described in detail to cover the broad spectrum where these coatings are used in preference to other engineering solutions.

4.1. Thermal barrier coatings for turbines

Thermal barrier coatings (**TBC's**) consist of alloys of **zirconia** with stabilising oxides such as **yttria**, magnesia, **calcium** and **ceria**. 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 a thickness of about 0.38 mm over the airfoil surface of turbine blades. It has been documented that the expected fuel efficiency is improved by several **percent**¹⁷; and therefore these coatings are placed on a sound economic basis for domestic applications such as aircraft and power generation. The thermal barrier effect can, on the other hand, allow the coatings to operate at higher temperatures and the benefit under these conditions is for increased performance of military aircraft.

It is generally accepted that the best TBC also has the most similar thermal expansion coefficient to that of the substrate. It is unlikely that any transformation toughening of the PSZ material plays a large role in enhancing the mechanical properties of the coating since the prior network of lamellar boundaries are pre-existing regions of weakness that determine the fracture path within the coating. Thus any potential toughening will always be restricted to the periphery of the splats and only a minimal amount is expected.

The ceramic overlay is used in conjunction with a 0.13 mm **NiCrAlY** bond coat to improve adhesion of the ceramic overlay. However it is believed that oxidation of the bond **coat**¹⁸ eventually leads to expansion stresses that cause the TBC system to **spall** under repeated thermal cycling. There is great interest at present to model this failure process so that the life time of the coating can be **predicted**¹⁹.

4.2. Wear resistance for turbines

Coatings which are based on WC-Co material composites are applied to the compressor fan and disc mid-span stiffeners to prevent wear; and to the compressor airfoils in order to control particulate **erosion**²⁰. These **coatings** are formed from cermet composite powders that are, in some cases, produced by a micro-pelletization process. The individual components of the powder consist of a hard phase which is dispersed within the matrix **component**²¹.

4.3. Abradable coatings in turbines

Some parts of aero-engines require good sealing between the rotating components to maintain high compression of gases. In these cases an **abradable** coating is formed on the stationary component, such as the compressor, and an abrasive material is coated onto the tip of the turbine **blade**^{20,22}. Thus the turbine will maintain the minimum clearance between the rotating components and thereby optimum operation of the engine is achieved. 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. Nichrome-bentonite composites have also been **found**^{20,23} to perform well in this application. The abrasive component of the system consists of a coating of alumina or of nichrome and chromium carbide.

4.4. Diesel engine applications

Thermal barrier coatings have also been used in diesel **engines**²⁴ under design specifications of a "break mean effective pressure" of 1.03 **MPa** and peak pressures of about 14 **MPa**²⁵. The **zirconia-yttria** alloy coatings are intended to improve fuel efficiency by insulating the combustion chamber area of the engine and 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 a thickness of 1.5 mm. The mechanical properties of the coating; such as adhesion to the substrate and thermal fatigue cycling resistance is optimum at the lower thickness²⁶. The improvement in fuel economy is about 1.5 to 3%. A molybdenum coating can be applied to piston rings to ensure long term sealing of the combustion **chamber**²⁷. It is believed that the coating after application contains some molybdenum oxide which improves the wear resistance of the coating; and if **30wt% NiCrSiB** is added to form a composite then the scuffing resistance is markedly improved.

4.5. Manufacture of near net components

The thermal barrier effect of ceramics is also taken advantage of in the use of alumina for **radomes**²⁸. These are the structural elements which are used to protect antennae on airborne vehicles. These engineering components can be sprayed onto a mold and then removed so that a free standing form is produced.

4.6. Bioceramic coatings

Coatings which are based on the apatite system have been used to improve the fixation of prosthetic appliances to the human **anatomy**²⁹. Ceramics such as hydroxyapatite can be thermal spray deposited onto the stems of artificial hips and then the engineering assembly directly inserted in the prepared femoral bone.

The prime advantage is there is no necessity to use an epoxy to glue the prosthesis into place. It has been established that the epoxy leads to necrosis of the immediately surrounding bone tissue and this may cause loosening of the prosthesis (and pain for the recipient) 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**³⁰. The chemistry of the coating duplicates that of the natural material and therefore there is no rejection of the appliance from the body. In the long term all of the thermally sprayed hydroxyapatite will gradually be reabsorbed and replaced by natural bone; that is, the appliance will become "**osteo-integrated**" to the natural bone. A very tight seating of the prosthesis in the bone bed is eventually achieved and this condition allows the best stress transfer from the appliance to the body.

It can be pointed out that this bioceramic application relies on two material properties which are usually thought of as being detrimental to the component life; these being the porosity and the environmental degradation. Thus in the above application a major design requirement is to manufacture a coating with a specific porosity size and

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distribution. It is also necessary for the coating to be gradually resorbed into the body so that natural osteo-integration can proceed.

These bioceramic coatings fall under the heading of intelligent materials since they are required to accommodate themselves with the operating environment for them to exhibit the greatest functionality. Thermally sprayed materials have also been investigated with a view to producing powders for filtration of blood plasma, or to manufacture industrial membranes for the petrochemical industry.

4.7. Superconductors

Much has been documented about the new **Y-Ba-Cu** high temperature superconducting materials since their formulation in the **mid-80's**³¹⁻³³. Thermal spraying is one popular method that has been used to manufacture components. The major problems in controlling the spraying process are **two-fold**; the powder preparation and the thermal spraying parameters to manufacture reliable coatings on a production basis. These limitations are discussed below to obtain a focussed view of the thermal spraying process.

The powders are manufactured by combining the oxides of yttrium, barium and copper in the ratio of **1:2:4**. The powders are generally in the size range of from 37 to 105 microns (ie, **+400** to **-140** mesh). During thermal spraying the copper oxide is preferentially lost so that the optimum **1:2:3** oxide ratio is achieved. It has been found that any particles that are less than 37 microns tend to lose copper preferentially and therefore these fine particles are considered detrimental to the production of coatings that have a reliable superconducting property.

Plasma spraying is the preferred technique since the lower temperature flame spraying process results in significant porosity and a mechanically weak coating. It is necessary to heat treat the coating (eg, for 20 hours at 950 C in flowing oxygen) before the superconducting phenomenon is observed.

4.8. Heavy industry applications

Thermally sprayed ceramics have found great utility in industrial applications and a selection of these will be presented. The most commonly used coatings are based on alumina.

Alumina, **alumina-zirconia** composites, alumina-magnesia (spinel), alumina-silica (mullite) and magnesium zirconate (**MgZrO₃**) have been **used**³⁴ 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. It is important to note that the requirement for a high bond strength is, by itself, not considered essential for the coating to **perform** satisfactorily since materials with strengths of 5 **MPa** have proved

satisfactory. The wear tests are performed at room temperature and there was some concern about their relevance for metallurgical vessels operating at **1500°C**; however the test (DIN 52108) was quite successful in screening the materials of interest.

Alumina, **alumina-rutile** and alumina-nichrome materials have been **used³⁵** to form coatings that extend the life of hot extrusion dies. The coatings have two main attributes; they prevent heat loss through the die during the extrusion process and they prevent wear of the die material. The outcome is an improvement in die life by a factor of 7 and improved productivity (it is claimed) by 100%; since production runs are not halted by frequent die changes. The product quality was also improved since the tolerances and surface finish of the product could be maintained for longer periods. The pure oxide coatings were less durable than the uncoated dies; whereas the optimum coating was a graded composite of alumina and nichrome. There were **no** special precautions to manufacture composite powders and the separate constituents were blended together prior to the thermal spraying operation.

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 rolls have usually been resurfaced with metals which are based on nickel and chromium alloys by manufacturing processes which include electroplating, fusion welding, cladding techniques and, more recently, thermal spraying. The thermal spraying of WC-Co materials by high velocity thermal spraying processes such as **D-gun³⁶** and **Jet Kote³⁷** has found increasing use since the late 1970's. The coatings so formed are excellent for **tribological** applications in 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 **lines³⁸**. These coatings successfully replaced electroplated chromium and they were superior to thermally sprayed carbide coatings. It was established that coatings of 0.2 mm in thickness exhibited an appropriate heat transfer coefficient to allow **uniform** cooling of the sheet steel product and were reliable in terms of good wear and thermal shock resistance.

Alumina and **rutile** have been plasma sprayed onto glass coated steel tanks to repair defects in the sodium-silicate **lining³⁹**. 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 ensure that the surface temperature of the substrate (ie, the silicate glass) was between 500 to **600°C**; and 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 unacceptably low due to thermal shock cracking of the silicate substrate. No bond coat procedures were necessary to obtain coatings of 0.3 mm thick.

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**⁴⁰ by the application of a three layer system of **metal-ceramic** composite materials. The initial layer which was applied directly to the copper tuyere was obtained by pack diffusion of aluminium and incorporated some embedded particles of alumina.. Then two layers were thermally sprayed and consisted 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**.

4.9. Power generation plant applications

The flame, plasma and arc metallization processes are well suited for the spraying of metal layers which prevent and control the high temperature corrosion in power generation plant applications^{41,42}. It can also be noted that thermally sprayed metals have been used to control radiation levels, by acting as a biological shield, in nuclear fuel processing facilities⁴³. The thermal spraying of ceramics and cermets has **also** found **application**⁴⁴ when they are sprayed by the **D-gun** process. 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 the **service** conditions to combat erosion due to fly ash.

4.10. Electrical industry applications

Ceramic coatings are not always primarily chosen to take advantage of their response to mechanical stress or their good resistance to adverse environments. For example the coatings may confer some specific electrical or magnetic property to the substrate. However it is still important for the coatings to adhere to the substrate and in many cases to tolerate adverse **thermo-mechanical** stresses.

Examples include the use of alumina which has been plasma sprayed onto an aluminium substrate to manufacture an acoustic **diaphragm**⁴⁵. The thermal spraying of **silicon**⁴⁶ has been used to produce poly-silicon coatings of type n and p which exhibited varying resistivity. These coatings may form the base material for a low cost solar **cell**⁴⁷.

Electrically insulative coatings have been fabricated out of alumina^{48,49}, spinel, cordierite and **forsterite**⁴⁹. On the other hand electrically conductive coatings subjected to adverse wear **environments**⁵⁰ have been manufactured from titanium diboride in aluminium bronze and zirconium carbide in aluminium bronze. The zirconium carbide in copper composite also demonstrated good conductivity.

Multi-component coatings have been used to manufacture a solid oxide fuel **cell**⁵¹. This coating consisted of layers of **LaCoO₃**; **LaCrO₃**; nickel-aluminium; nickel-aluminium and calcia stabilized zirconia; and **yttria** stabilised zirconia which were sequentially sprayed onto an alumina tube. The electrolyte of **yttria** stabilized zirconia needed to be impermeable and therefore it was produced by a plasma method; whereas the electrode

of LaCoO_3 required gas permeability and this was manufactured by a flame spraying method. The fabrication of the fuel cell by thermal spraying techniques was reasonably successful; however improvements in the coating definition and its tolerances are thought to be necessary before this technology can be implemented.

5. CONCLUDING REMARKS

The applications of thermal spray technology are many and varied; and this review has focussed on several which were aimed at preventing and controlling mechanical, thermal and **tribological** degradation. Thermal spray coatings are sometimes disadvantaged as a process since they are formed by a line-of-sight process and therefore the engineering component may not be suited for the intended coating process. Generally if the component can be grit blasted, the prerequisite surface treatment prior to thermal spraying, then the component can probably be surfaced. The surface finish after grit blasting is also quite typical of the finish of a coating; however the coating may be post-processed if required and if the additional machining cost can be borne by the customer. In some instances the thermal spray coating can be applied in the field or without removal to a specialized reclamation facility. It is becoming more common though for the coatings to become incorporated into the component at the design stage and this results in significant economic gain.

There are many processes in the family of thermal **spraying**¹⁶ and all of these may have specialized applications. For example flame spraying is an inexpensive process that is well suited for metallic materials whereas the **D-gun** is best suited for WC-Co materials that are used for wear applications; although it can be noted that it is best to spray some materials (for example bond coats that are intended for high temperature application) by using low pressure plasma technology. Ceramics are most generally sprayed by the higher temperature, higher velocity processes such as, for example, plasma, D-gun and Jet Kote.

It is difficult in some respects to separate metal and ceramic applications for thermally sprayed coatings since these materials are often used together. The metal may act either as a bond coat so that adhesion of the coating system to the substrate is improved or the metal can be co-sprayed with the ceramic to form a cermet composite. The powders^{21,52,53} may be either premixed in a mechanical fashion; a composite powder can be manufactured which has the different components bound together in each powder particle; or two different powder delivery systems can be used to feed the powder to the thermal spraying torch. Another more recent technique is to manufacture a ceramic-ceramic composite which incorporates one of the ceramics in the physical shape of a **continuous**⁵⁴ or **discontinuous**⁵⁵ fibre.

An important consideration to remember is that the coating microstructure and phase **distribution** are dissimilar to that of the bulk constituents. These morphological

aspects of ceramic coatings control the material properties; such as thermal diffusivity, mechanical strength in tension and shear, and wear characteristics; and therefore they influence their utility. It is only by a systematic approach in investigating the **processing/structure/property** relationships that future development and applications of coatings can take place.

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