Plasma- Spray Coating

by. Robert B. Heimann

1 Introduction

Thermal spraying has emerged as an important tool of increasingly sophisticated surface engineering technology. Research and development are increasing rapidly, and many applications are being commercialized. An indication of this rapid development is the fact that over 80% of the advances made over the last 90 years were made in the last two decades, a corollary to Pareto's 80/20 rule! [1] Many exciting niches are opening up for metallic and ceramic surface coatings that include such well established markets as aerospace and consumer industries but also more slowly developing coating markets in the automotive, computer and telecommunications industries.

The goal of this text is to give students and researchers in materials engineering and materials science an appreciation of the fundamental physical processes governing plasma spray technology, to provide familiarization with advantages and disadvantages of the technology compared to other surface coating techniques, to discuss basic equipment requirements and limitations, to present case studies and typical applications of plasma spray technology to solve industrial problems, and to lay a foundation for future research and development work in this field.

The material covered will discuss the basic nature of the plasma state, plasma–particle interactions, heat and momentum transfer, particle–substrate interactions, analyses of the microstructure, adhesion strength and residual stresses of coatings, optimization of coatings by SDE (statistical design of experiments) and SPC (statistical process control) methods, modeling of the plasma spray process, and an account of a novel fractal approach to coating properties, and other nonlinear considerations. The fundamental physical processes underlying plasma spraying have been treated in detail. It was felt that many other texts neglect this topic even though this knowledge is crucial to the understanding of the process and, most importantly will enable the materials and maintenance engineer to choose the most appropriate combination of materials, equipment and parameter selection to lay down coatings with high performance, new functional properties, and improved service life.

It should be emphasized, however, that this text can not cover the totality of this fast developing field. In particular, limitations on space and reliable information, and the wide variety of types of equipment and coatings as well as applications, prevented covering some aspects of plasma spray technology in detail. For those reasons, differences in the type of plasma spray systems used successfully in many applications have not been given much consideration. However, the following text will give brief references to the most pertinent aspects of plasma spray technology, and will enable the reader to build on this knowledge in order to perform research and development work.

Collaboration between universities or government research organizations and industry in the resource and manufacturing sectors will lead increasingly to strategic alliances that enable industry to perform more competitively and in an environmentally compatible way within the framework of a global concept of sustained development. Process control, including 3D-modeling of complex plasma–particle–substrate interactions, on-line process diagnostics, and development of novel coatings with improved performance are areas rich in research needs and opportunities. Specialists in plasma processing, including plasma spray technology, will find a rewarding field of endeavour in the 1990s and beyond.

1.1 Coatings in the Industrial Environment

There is increasing worldwide interest in thermal spray coatings. According to a study conducted by the Gorham Advanced Materials Institute [2], the sales of advanced ceramics are expected to topple US $4 billion in 1995, 80% of which will be in ceramic coatings (Figs 1-1, 1-2). The 1986 world sales for ceramic coatings (total sales: US $1.1 billion) were achieved predominantly in the construction industry (36%), metal fabrication industries (21%), military (12%), and other industries (31%): chemical processing, internal combustion engines, petrochemical and metal producing industries. Of the ceramic coatings, 39% were produced by physical vapor deposition techniques (PVD), 26% by chemical vapor deposition (CVD), 23% by thermal spraying, and 12% by wet processing including sol–gel technique [3]. Recent predictions show that these markets are expected to triple to more than US $3 billion by the year 2000 with an annual average growth rate of 12%. The industrial segments with the largest predicted individual annual growth rates are engines (28%), marine equipment (18%), chemical processing (15%), military (11%)[1], and construction (11%). A field of application with a large potential is bioceramic coatings based on plasma-sprayed hydroxyapatite. Such biocompatible coatings for prosthetic implants in bone promise to have a rapidly growing market in an aging population [4]. High-temperature superconductive and diamond coatings are on the verge of making technological breakthroughs in the microelectronics industry [5].

Besides high-technology applications a major market exists in the resource industries including oil and gas, mining, forestry, pulp, paper and agricultural industries, manufacturing and electronics, automotive and aerospace industries. In partic-

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[1] This figure does not contain a presumed reduction in spending caused by the recent reduction in political tension between the two large military blocks.

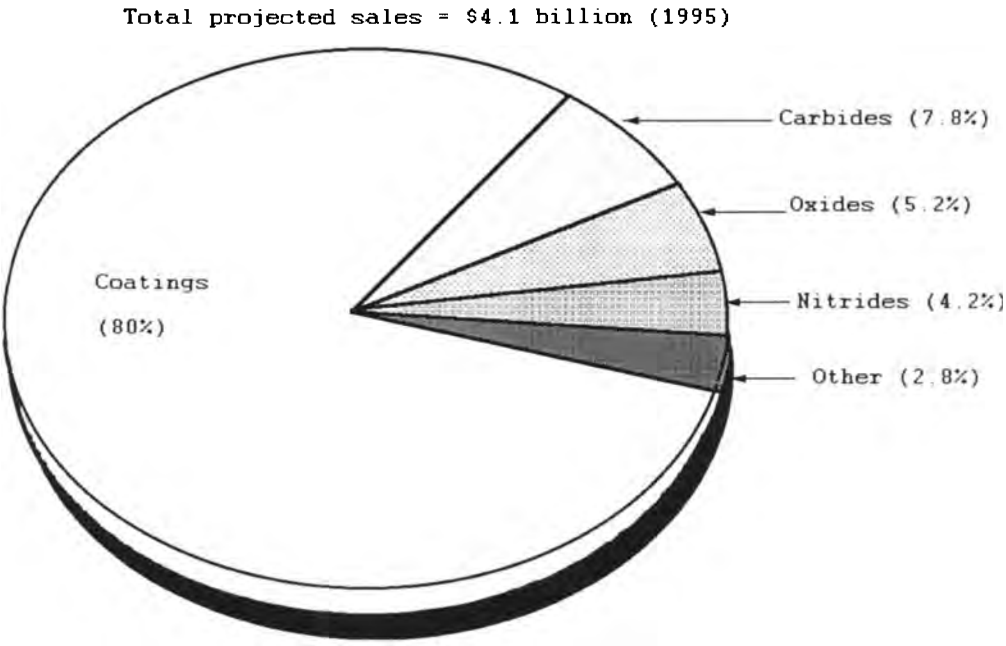

Figure 1-1. Forecast of worldwide sales in advanced structural ceramics and ceramic coatings [2].

ular, industries threatened by international competition, erosion of raw material prices, and shifts to new materials and technologies must radically improve operational efficiency, industrial diversification and environmental compatibility to survive. An important contribution in this struggle can be made by coatings that combat wear, erosion and corrosion found at all levels of operations in industry, that impart new functional properties, extend the service life of machinery, and contribute in general to sustainable development required by the increasingly environmentally conscious world of the decades to come.

The market development of ceramic coatings depends to a large extent on individual products that must, in terms of materials and technology alternatives, show better performance than competing materials. The field of application of the product appears to be less important. Figure 1-3 shows that the onset of substantial market penetration in automotive applications is considerably earlier for ceramic coatings than for monolithic ceramics and ceramic composites [6].

1.2 Surface Coating Techniques

Before providing details on plasma spray technology, and the wide field of applications of plasma spray-generated surface coatings, a short review will be given of

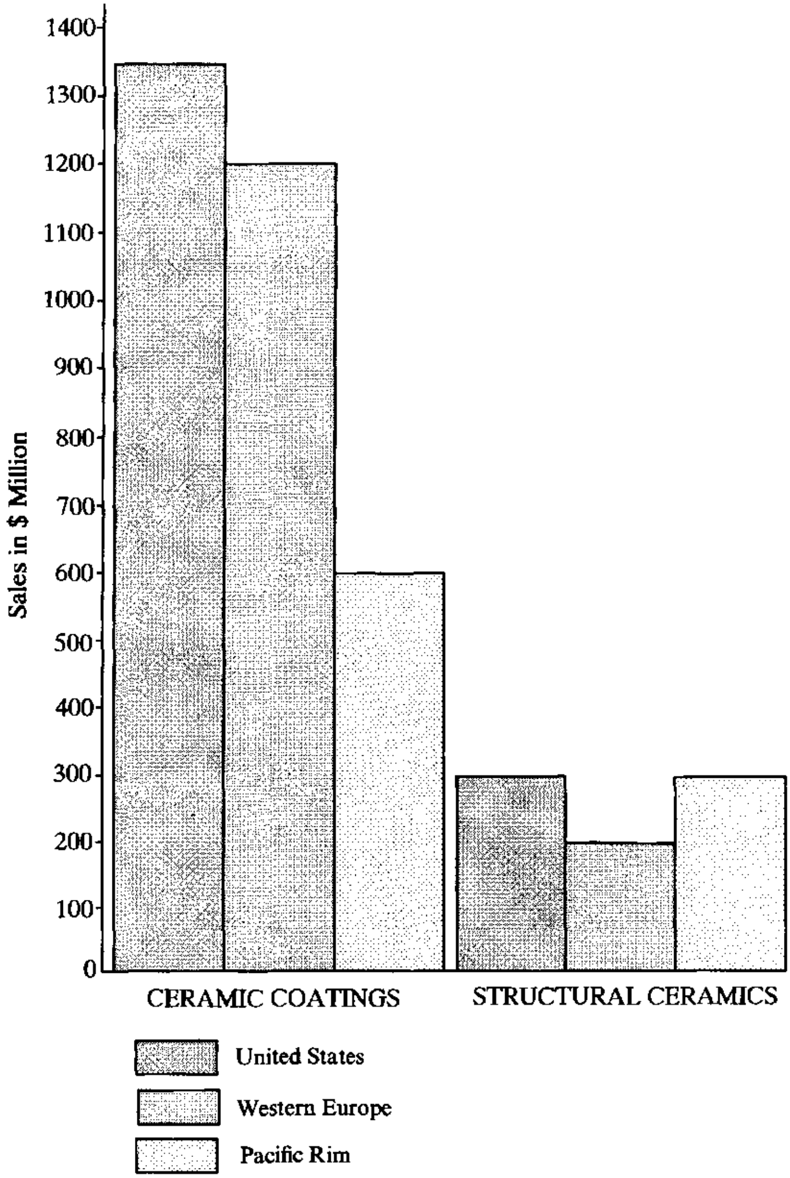

Figure 1-2. Forecast of worldwide sales of advanced structural ceramics and coatings by region [2].

various other surface coating techniques. More details can be found in the literature [7, 8].

The advantage of coating technology, in general, is that it marries two dissimilar materials to improve, in a synergistic way, the performance of the whole. Usually mechanical strength and fracture toughness are being provided by the substrate and

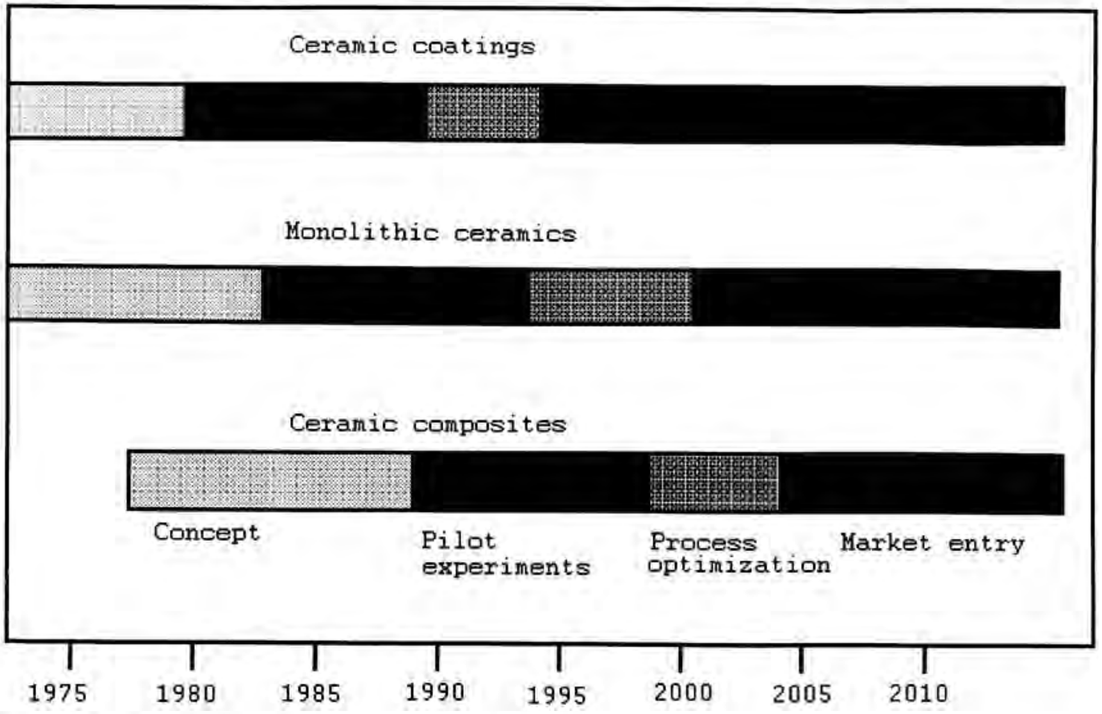

Figure 1-3. Development stages of ceramic engine parts [6].

the coating provides protection against environmental degradation processes including wear, corrosion, erosion, and biological and thermal attack.

Surface coating technologies have the following advantages.

- *Technical advantages.* Creation of new materials (composites) with synergistic property enhancement, or completely new functional properties, for example electronic conductivity, piezo- or ferroelectric properties etc.
- *Economic advantages.* Expensive bulk materials such as stainless steel or superalloys can be replaced by relatively thin overlays of a different material. These savings are enhanced by longer life time of equipment and reduced downtime and shortened maintenance cycles.
- *Attitudinal advantages.* Materials engineers trained in metals handling need not be afraid to deal with new materials with unfamiliar properties, specifications and performance such as ceramics or polymeric composites. The ceramic coating just becomes a part of a familiar metal materials technology.

Coatings are, of course, not a new invention. For times immemorial, wood and metal have been painted with organic or inorganic pigments to improve their esthetic appearance and their environmental stability. Corrosion-, wear- and abrasion-resistance of the substrate materials were significantly improved by the paint coatings. These organic paint coatings, however, did not endure high temperatures and did not adhere well. The performance of traditional coatings has been improved by the use of chemically-cured paints in which components are mixed prior to application and polymerized by chemical interaction, i.e. cross-linking. Epoxy resins, polyurethanes and various polyester finishes show considerable resistance to alkalis and acids, and also to a wide range of oils, greases and solvents.

Traditional enamels are glass-based coatings of inorganic composition applied in one or more layers to protect steel, cast iron or aluminum surfaces from corrosion. This technology has been extended today to manufacture thick film electronics in which metals or metal oxides are added to a fusible glass base to generate a range of thick film conductors, capacitors and other electronic components.

Chemical coatings are frequently applied by electroplating of metals such as copper and nickel. Nickel, for example, forms a highly adherent film for wear applications by an electroless plating process, and thus is applied to manufacture aerospace composites. A related technology is the anodizing of aluminum by electrochemically induced growth of aluminium oxide in a bath of sulphuric or phosphoric acids. *Spray pyrolysis* involves chemical reactions at the surface of a heated substrate. Increasingly transparent conducting coatings of tin oxide or indium tin oxide are used to coat glass windows for static control, radio frequency shielding and environmental temperature control.

Sol–gel coatings based on the pyrolysis of organometallic precursors such as metal alkoxides are used today. The process was originally developed for aluminum and zirconium oxide but is now extending to a wide range of glasses including silicates and phosphates, and has recently been applied to complex ferroelectrics such as PZT (lead zirconate titanate) and PLZT (lead lanthanum zirconium titanate). Sol–gel coatings enjoy a high compositional flexibility and ease of preparation at generally ambient temperature but because of the frequently expensive precursor materials their application is limited to high-value added devices, in particular in electronics.

Thin coatings produced by CVD are widely employed in the semiconductor industry for large band-gap materials such as gallium arsenide, indium phosphide and other compound semiconductor materials. The technology uses vapor phase transport to grow epitaxial and highly structured thin films including insulating oxide films on single crystal silicon substrates. A related technology is the growth of thin crystalline diamond films by decomposition of methane or other hydrocarbons in a hydrogen($>95\%$)–argon($<5\%$) plasma. Much activity is currently devoted in Japan and the USA to the improvement of the thickness and the crystallographic perfection of diamond thin films. Major potential industrial applications of such films can be found for protective coatings on compact discs, optical lenses, in particular such carried by low-earth orbit space craft, and substrates for ULSI (ultra large scale integration) devices.

Physical Vapor Deposition (PVD) technologies using evaporation, sputtering, laser ablation, and ion bombardment are a mainstay of present-day surface engineering technology.

Evaporation is the most simple vacuum technique. The materials to be deposited on a substrate are melted and vaporized either on a resistively heated tungsten or molybdenum boat, or by an electron beam. The method is suitable for many metals, some alloys, and compounds with a high thermal stability such as silica, yttria and calcium fluoride. While films deposited by evaporation are inferior to other vacuum techniques in terms of adhesion to the substrate, the excellent process control generating optical films with well-defined thicknesses and indices of refraction has made this technique popular.

Sputtering methods deposit material by causing atoms to separate from a target by bombardment with highly energetic ions from a gas plasma or a separately exited ion beam, and depositing them on a substrate. Magnetron sputtering uses confinement of the exiting plasma by a strong magnetic field that results in high deposition rates and good reproducibility. Large area sources are used to coat plastic foils and ceramic substrates for packaging materials in the food industry, as well as for metallizing plastic ornaments and automotive components such as bumpers, for architectural glass, and for multilayer holographic coatings on identification and credit cards to prevent forgeries.

Laser ablation is a modern technology that has been developed in particular for high temperature superconducting ceramics. A focused laser beam is used to vaporize the target material. Since this material comes from a highly localized region the ion flux reproduces the target composition faithfully. Even though the cost of the lasers is still high and the deposition rates are quite low, future developments may lead to much wider application of this technique if reproducible process control can be achieved.

The PVD methods mentioned so far all rely on a coating deposited on an existing substrate surface with given composition. However, *ion implantation* modifies the properties of the substrate itself. A beam of high energy ions can be created in an accelerator and brought in contact with a substrate surface. Thus corrosion and wear performance can be improved dramatically. For example, implantation of 18%

chromium into a steel results in an *in-situ* stainless steel with high corrosion resistance, the use of boron and phosphorus produces a glassy surface layer inhibiting pitting corrosion, and the implantation of titanium and subsequent carbon ions creates hard-phase titanium carbide precipitates. Likewise implantation of nitrogen produces order of magnitude improvement of the wear resistance of steel, vanadium alloys, and even ceramics.

Modern high performance machinery, subject to extremes of temperature and mechanical stress, needs surface protection against high temperature corrosive media, and mechanical wear and tear. For such coatings a highly versatile, low cost technique must be applied that can be performed with a minimum of equipment investment and does not require sophisticated training procedures for the operator. Such a technique has been found in thermal spraying. It uses partially or complete melting of a wire, rod or powder as it passes through a high temperature regime generated electrically by a gas plasma or by a combustion gas flame. The molten droplets impinge on the substrate and form the coating layer by layer. This technique is being used widely to repair and resurface metallic parts and also, in recent years, to build up wear-, chemical- and thermal barrier coatings based on alumina or zirconia, in particular for applications in the aerospace and automotive industries. High temperature-erosion protection of boiler tubes and fire chambers of coal-fired power plants, corrosion protection of special concrete parts, and of bioceramic coatings for orthopedic and dental prosthetic implants are just a short list of ever increasing fields of service of thermally sprayed coatings.

For all these reasons, advanced materials, i.e. ceramics or polymer coatings, become more and more popular among materials engineers. The equipment, ease of application of coatings to complex surfaces, and the availability of tailored materials makes novel surface coatings increasingly attractive. Thus it has been said that coatings technology will be the materials technology of the 21st century.

1.3 Brief History of Thermal Spraying

After several patents in 1882 and 1899, in 1911 M. U. Schoop in Switzerland started to apply tin and lead coatings to metal surfaces by flame spraying to enhance corrosion performance [9]. The field developed quickly, and in 1926 a comprehensive book was published by T. H. Turner and N. F. Budgen called *Metal Spraying.* A new edition was published in 1963 with the title *Metal Spraying and the Flame Deposition of Ceramics and Plastics* to reflect the shift from metals to other materials.

Figure 1-4 gives an impression of the pace of development of thermal spray technology [10]. It illustrates those applications that have been either motivated or made possible by the technological progress (see, for example [11]) and shows advances being led by entrepreneurs or companies. The curve follows a typical life-cycle curve: slow at first after inception by Schoop in 1911, and then increasing at a modest rate until the late 1950s. At this time the appearance of a variety of then-modern plasmatrons boosted the development considerably. In particular, the D-gun coatings

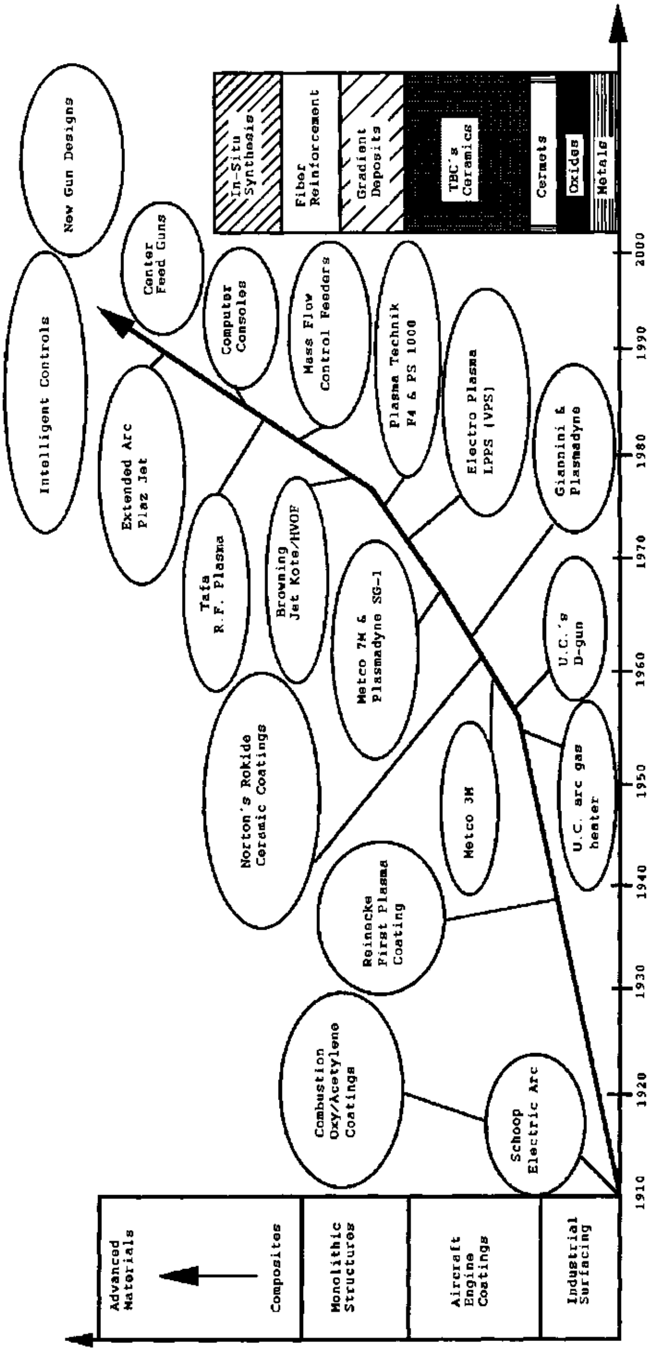

Figure 1-4. Thermal spray technology growth: summary and milestones [10]; UC = Union Carbide Co.

(Praxair Surface Technology, Inc., Indiannapolis, IN, USA) applied by the Union Carbide Corporation found a receptive market in the aerospace industry, and a large proportion of the subsequent technological growth was due to plasma-sprayed thermal barrier coatings based on stabilized zirconia. The second growth spurt shown in the figure occured in the 1980s with the invention of the vacuum plasma spraying/low pressure plasma spraying (VPS/LPPS) and the Jet Kote/hypervelocity oxyfuel gun (HVOF) techniques and the high temperature-coatings for aerospace gas turbine associated therewith shown in Fig. 1-5, [12]. (Jet Kote is manufactured by Browning Engineering, Enfield, NH, USA.) Future developments, undoubtedly highlighted by a further increase in the rate of technological innovation, will probably include improved on-line real-time feedback control, intelligent SPC, design of new equipment and spray powders as well as 3D-process modeling and improved understanding of the complex nonlinear physics underlying the plasma spray process.

In the last two decades there has been increasing interest in coatings from the military and commercial sectors, leading to a wealth of information. Journals totally dedicated to thermal spraying exist, for example the *Journal of Thermal Spray Technology* (ASM), and biennial national and triennial international conferences present ongoing worldwide university and industry research and development efforts in a wide variety of thermal spray processes. Figure 1-6 illustrates these trends by showing the exponential growth of papers published between 1967 and 1991; Fig. 1-7 shows the number of papers presented and the number of attendees at the seven International Metal Spray Conferences (1956 to 1973) and seven International Thermal Spray Conferences (1976 to 1995) held so far [13]. Again, the number of papers, Y, follows an exponential growth law, $Y = 19.7 \exp(0.05X)$ with a correlation coefficient $r = 0.96$, where X is the year measured from the inception of the international conferences.

Activities are well underway to develop expert systems that integrate exhaustive databases with expert knowledge and practical experiences. For example, powerful software has been developed that allows the engineer to determine the best coatings for a given part or application, as well as information on how and where the coatings are being used. This database provides detailed information on over 1300 thermal spray applications and contains a listing of international suppliers. The materials covered are categorized into 12 groups including iron-based materials, nickel-based materials, cobalt-based materials and non-ferrous metallic-based materials [14]. Process simulation plays an increasingly important role in estimating the interdependence of spraying parameters and desired coating properties [15].

The main activities today center around:

- improving powder feedstocks, spray application equipment, and process control through SDE, SPC, and quality function deployment (QFD) techniques,
- designing new control devices, real-time feedback looping, mass flow controllers, powder metering equipment, manipulators and robots [16],
- effective innovation and technology transfer from research organizations to small and medium-sized enterprises (SMEs) [17] and
- development of data bases and expert systems [18].

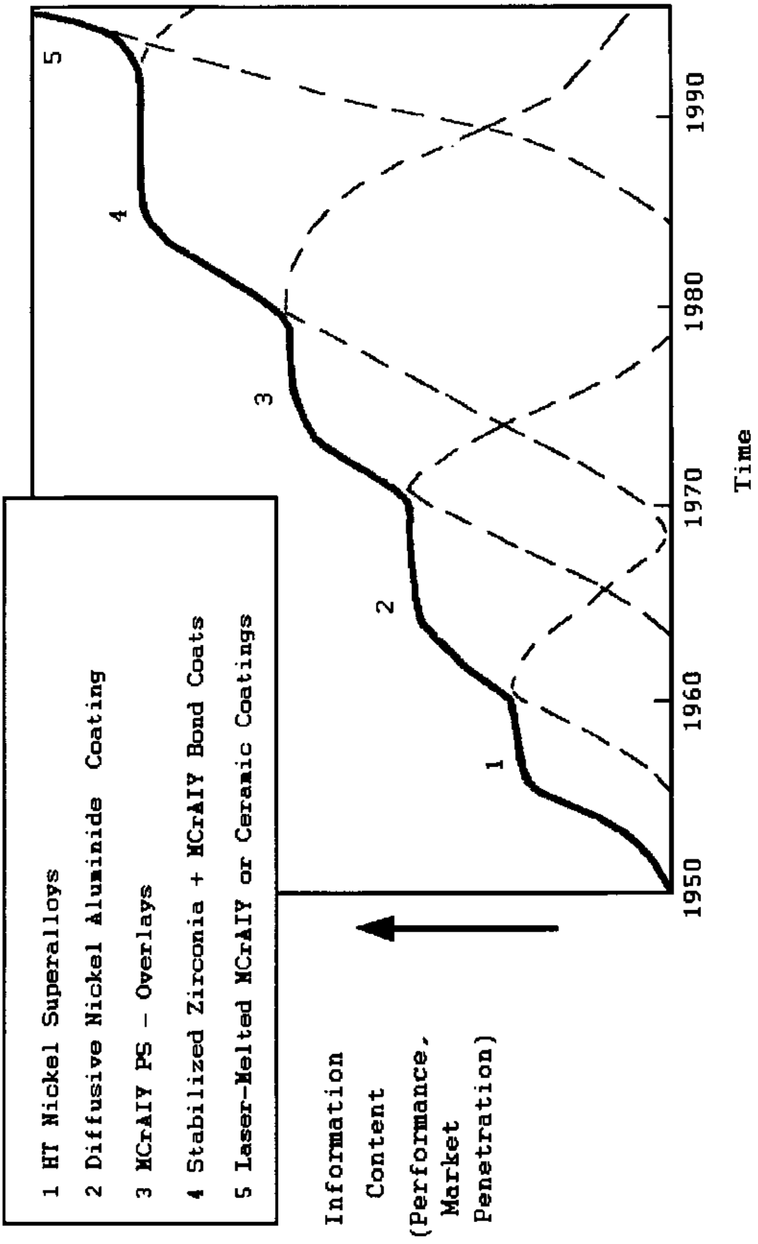

Figure 1-5. Evolution of high temperature coatings for gas turbines [12]: HT = high temperature, PS = plasma spray.

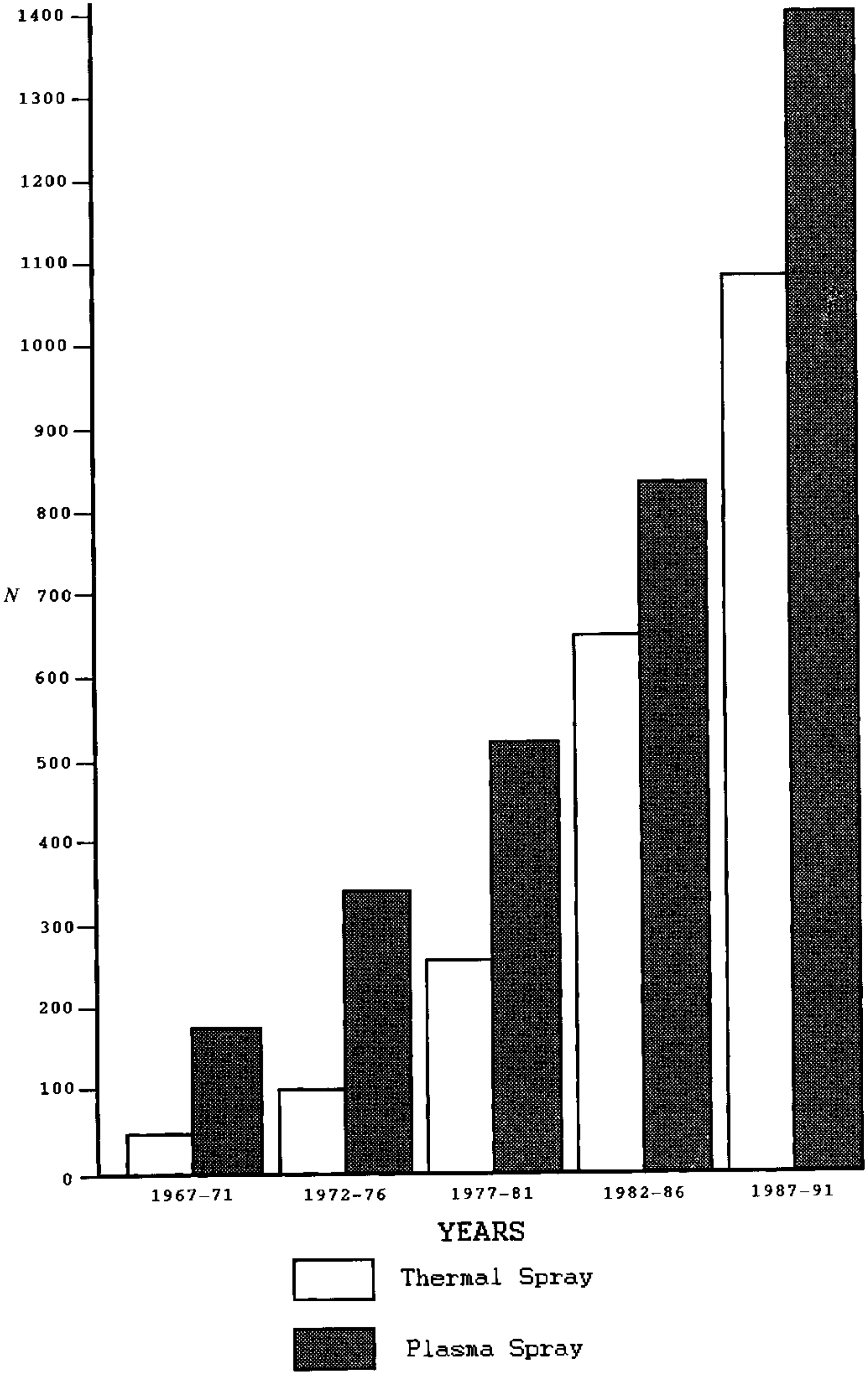

Figure 1-6. Exponential growth of research papers on thermal spray technology (1967–1991).

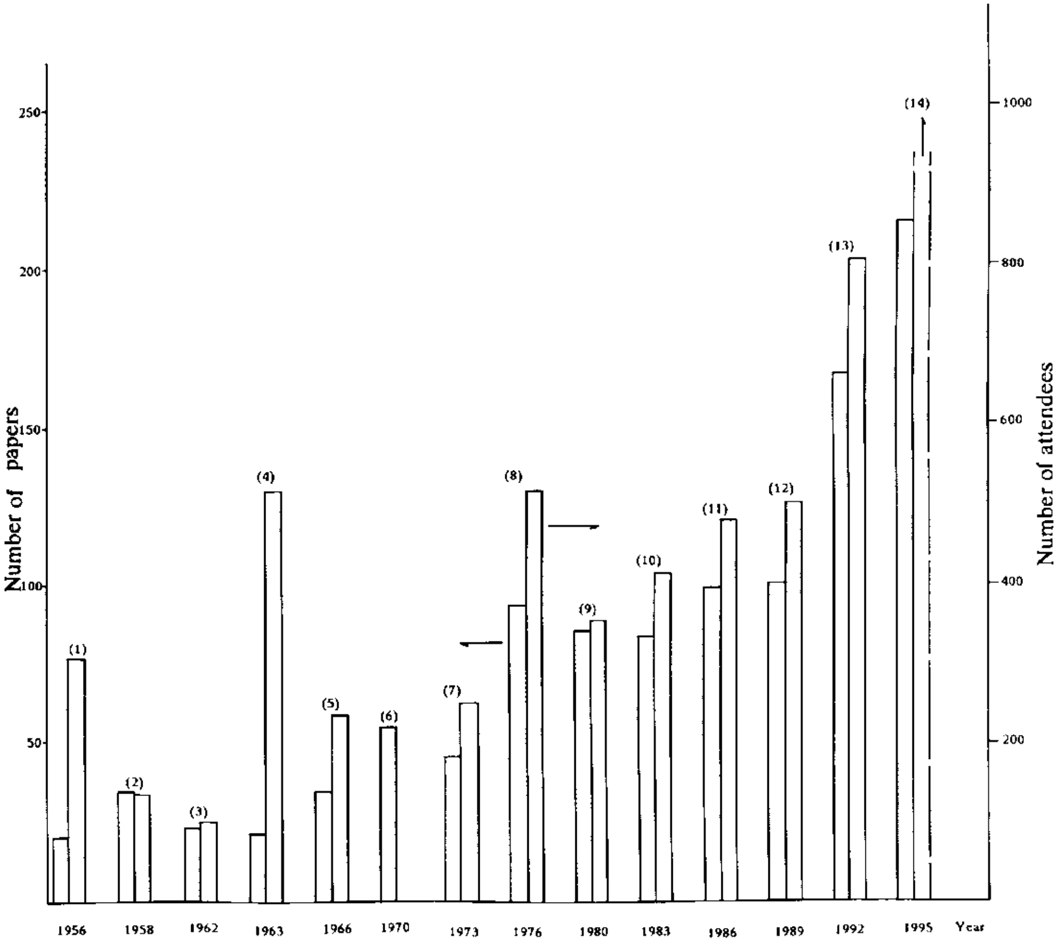

Figure 1-7. Exponential growth of papers presented (left bar) at International Metal Spray Conferences (1956–1973) and International Thermal Spray Conferences (1976–1995), and number of attendees (right bar) [13].

1.4 Synergistic Nature of Coatings

A metal substrate/ceramic coating system combines the mechanical strength of a metal with the environmental stability of a ceramic material. Typical metal properties exploited are:

- creep strength,
- fatigue strength,
- flexural strength,
- ductility,

- high fracture toughness,
- high coefficient of thermal expansion,
- high heat conductivity, and
- low porosity.

Typical ceramic properties are:

- high thermal stability,
- chemical stability,
- high hardness,
- low fracture toughness,
- low coefficient of thermal expansion,
- low heat conductivity, and
- medium to high porosity.

The combination of these properties yields a superior composite material. However, several aspects have to be carefully controlled such as the difference between coefficients of thermal expansion of metal and ceramic which leads to undesirable stresses at the substrate–coating interface. Also, the generally high porosity of plasma-sprayed ceramics has to be dealt with by either infiltrating the coating with another material, hot isostatically pressing, or by laser densification or other techniques. The low fracture toughness of the ceramic is also of concern. Intense research is ongoing worldwide to develop ceramics with improved fracture toughness. For example, research is being pursued to thermally spray fiber-reinforced ceramics, such as silicon carbide–alumina composite coatings.

1.5 Applications of Thermally Sprayed Coatings

There is an ever increasing number of technical applications of plasma-sprayed metal and ceramic coatings. Many of such applications have resulted from the demand from the users of machinery and equipment to protect their investment from wear, corrosion, erosion, and thermal and chemical attack. Others result from the desire to impart new functional properties to conventional materials, such as high-temperature superconducting coatings, bioceramic coatings, diamond coatings, and electrocatalytic coatings for solid oxide fuel cells (SOFCs). It is not possible to cover here all applications of thermally sprayed coatings. The list below shows but a few industrial areas where coatings have been successfully used to solve performance problems. Practical solutions to a specific problem frequently follow a well-established sequence of events [19]:

- problem identification,
- specification of coating properties,
- proposed solution including selection of materials to be sprayed, equipment and technique used etc.,

- application of coating, and
- evaluation of results in terms of technical performance and economic viability.

Typical applications of metallic and ceramic coatings are:

- wear and erosion control of machinery parts and turbine vanes, shrouds and blades in coal-fired power generating stations;
- particle erosion control in boiler tubes and superheaters of coal-fired power plants;
- chemical barrier coatings for ethane steam cracking furnace tubes for coking and erosion protection;
- wear control and improvement of friction properties in a variety of machine parts, including pump plungers, valves, bearings, and calender and printing rolls;
- metal coatings for corrosion protection of engineering structures such as steel and concrete bridges in coastal regions;
- corrosion protection against liquid metals in extrusion dies, ladles and tundishes;
- corrosion protection of equipment for petrochemical and chemical plants, and high-temperature corrosion in internal combustion engines;
- thermal and chemical barrier coatings for pistons and valves in adiabatic diesel engines and related machinery, as well as for aerospace gas turbine blades and combustor cans;
- resurfacing of worn equipment, for example in railway applications, ship building and maintenance, and mining tools and equipment;
- superalloys for aerospace gas turbine vanes and shrouds to prevent hot gas erosion and corrosion;
- ceramic membranes for osmotic filtering and ultrafiltration;
- biomedical coatings for orthopedic and dental prostheses with biocompatible properties based on hydroxyapatite and tricalcium phosphate;
- stabilized zirconia electrolyte and electrocatalytic active compound coatings for SOFCs;
- high-temperature superconducting coatings for electromagnetic interference (EMI) shielding;
- abradable coatings and seals for clearance control in gas turbines;
- coatings to protect concrete floors from corrosive action of fruit juices and other agricultural products;
- sealing of concrete floors in dairy industrial operations;
- thick metal overlays for PVD sputter targets; and
- diamond-like coatings for wear applications and for heat sinks in high-power electronic chips.

Some of these applications are dealt with in more detail in Chapter 6.

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