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 truly unique corollary to Pareto's 80/20 rule! (Alf, 1988). Many exciting niches are now being filled for metallic and ceramic surface coatings that include such well established markets as aerospace, energy and consumer industries but also developing coating markets in the automotive, computer and telecommunication industries. The particularly important segment of biomedical coatings for implant is today served by a variety of coating technologies with atmospheric plasma spraying (APS) still the leading contender.

The goal of this text is to give materials engineering/materials science students, mechanical and chemical engineers, researchers in the field of physics, chemistry and materials science, and last but not least spray shop managers, supervisors and foremen an appreciation of the fundamental physical processes governing plasma spray technology; to provide familiarization with advantages and disadvantages of the technology compared with 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 in general 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, an account of a novel fractal approach to coating properties and other nonlinear considerations. The fundamental physical processes underlying the plasma spray process have been treated in some detail since it was felt that other existing texts frequently neglect this topic. However, its 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

Plasma Spray Coating: Principles and Applications. Robert B. Heimann

ISBN: 978-3-527-32050-9

parameter selection to lay down coatings with high performance, new functional properties and improved service life.

It should be emphasized, however, that this text will in no way cover the totality of this fast developing field. In particular, limitations on space and proprietary information, and the wide variety of types of equipment and coatings as well as applications, prevented detailed treatment of some aspects of plasma spray technology. 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 generic research and development work.

Collaboration of universities and government research organizations with industry in the resource and manufacturing sectors will lead increasingly to strategic alliances that enable industry to produce in a more competitive and environmentally compatible manner within the framework of a global concept of sustained development. Process control, including three-dimensional (3D) modeling of complex plasma–particle–substrate interactions, on-line process diagnostics, and design and development of novel coatings with improved performance using knowledge-based analysis by artificial neuronal network and fuzzy logic control tools are areas rich in research needs and opportunities. Specialists in plasma processing including plasma spray technology will find an ever increasing rewarding field of endeavor.

1.1 Coatings in the Industrial Environment

1.1.1 Market Position

There is increasing interest worldwide in thermal spray coatings. The 1986 global 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%) including chemical processing, internal combustion engines, petrochemical and metal producing industries. 39% of the ceramic coatings 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 (Chan and Wachtman, 1987). At this time predictions showed that these markets were expected to triple to more than US$ 3 billion by the year 2010 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%) and construction (11%).

According to a study conducted by the Gorham Advanced Materials Institute 1990, the sales in advanced ceramics were predicted to top US$ 4 billion in 1995, 80% of which was supposed to be in ceramic coatings. While these predictions overestimated the actual growth rate by close to 100% (Gorham Advanced Materials

Institute, 1999), the real growth is still impressive. For example, the global thermal spray market for the year 2003 consisted of the following market segments: original equipment manufacturers and end users: US$ 1.4 billion; large coating service companies: US$ 0.8 billion; small coating service companies: US$ 0.6 billion; powder and equipment sales: US$ 0.7 billion. This adds up to a total of US$ 3.5 billion as estimated by Read 2003. This figure has increased to US$ 5 billion in 2004 of which 45% were obtained by atmospheric DC plasma spray technology (Fauchais *et al.*, 2006).

A field of application with a large potential are bioceramic coatings based on plasma-sprayed hydroxyapatite and second-generation bioceramics. Such biocompatible coatings for bone implants have promising applications to solve health problems of an aging population (Hench, 1991). High-temperature superconductive and diamond coatings as well as electrode and electrolyte coatings for solid oxide fuels cells (SOFCs) are on the verge of making technological breakthroughs in the microelectronics and power industries (Heimann, 1991a; Müller *et al.*, 2002).

Besides these high-technology applications a major market exists in the resource industries including oil and gas, mining, forestry, pulp and paper and agricultural industries, construction, manufacturing and electronics, automotive and aerospace industries. In particular, industries threatened by international competition, erosion of raw materials prices, and shifts to new materials and technologies must radically improve operational efficiency, industrial diversification and environmental compatibility to survive. An important component of this struggle are coatings that combat wear, erosion and corrosion found at all levels of operations in industry, that impart new functional properties, extent the service life of machinery, and contribute in general to the sustainable development required for the increasingly environmentally conscious world in the decades to come. Just to give an impression on the economic scale, in Germany alone, wear and corrosion of technical systems destroy annually the equivalent of about 4.5% of the GNP, corresponding to €35 billion (Henke *et al.*, 2004).

The market development of ceramic coatings depends to a large extent on individual products that must, in terms of materials and technology alternatives, show a better performance than competing materials. The field of application of the product appears to be less important. Figure 1.1 shows that the onset of substantial market penetration in automotive applications was considerably earlier for ceramic coatings than for monolithic ceramics and ceramic composites (Reh, 1989; Maier, 1991). More recently, applications of thermally sprayed coatings designed to meet today's environmental requirements for nonferrous engine blocks, hybrid solutions for aluminum automotive engines and coatings for engine cylinder bores for both gasoline and diesel engines have been highlighted by Barbezat (2002, 2005) (see also Woydt *et al.*, 2004).

1.2 Survey of 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

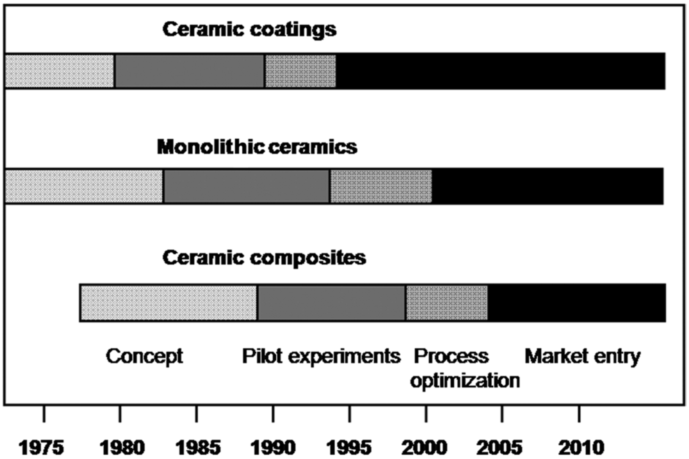

Figure 1.1 Development stages of ceramic parts for automotive engines (Reh, 1989; Maier, 1991).

various other surface coating techniques. For more details see, for example Bunshaw 1982, Sayer 1990 and Fauchais *et al.*, 2006.

The advantage of any coating technology in general lies in the fact that it marries two dissimilar materials to improve, in a synergistic way, the performance of the 'tandem' substrate/coating. Thereby mechanical strength and fracture toughness are provided by the substrate whereas the coating provides protection against environmental degradation processes including wear, corrosion, erosion, and biological, environmental and thermal attack.

There are three main advantages in using modern surface coatings technology.

- *Technical advantages:* Creation of 'new' materials (composites) with synergistic property enhancement, or completely new functional properties, for example electronic conductivity, piezo- or ferroelectric properties, electromagnetic shielding, bioconductivity and so on.
- *Economic advantages:* Expensive bulk materials such as stainless steel or Ni-based superalloys can be replaced by relatively thin overlays of a different material. These savings are enhanced by longer life 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, polymers or their composites. The thin ceramic coating added to a metal substrate just becomes a part of a familiar metal materials technology. However, increasingly protective coatings are considered 'prime reliant' components that are included *a priori* in the design, not as add-ons. This is happening predominantly in the aerospace and automotive industries where novel stringent quality requirements call for enhancement of both reliability and reproducibility of coatings. This necessitates a concerted, integrated interdisciplinary

approach for each specific system of coating technology and material. Among other routes process mapping is a valiant vehicle to establish and verify correlations among intrinsic and extrinsic spray parameters and coating performance (for example Sampath *et al.*, 2003; Chapter 11.1.4).

Coatings are, of course, not new inventions. Since time immemorial, wood and metals have been painted with organic varnish or inorganic pigments to improve their esthetic appearance and enhance their environmental stability. Corrosion, wear and abrasion resistance of the substrate materials were significantly improved by such organic *paint coatings*, however, they did not adhere well nor survive high temperatures. The performance of traditional coatings has been extended by the use of chemically-cured paints in which components are mixed prior to application and polymerized by chemical interaction, that is, cross-linking. Epoxy resins, polyurethane 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 that are designed 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 anodization of aluminum by electrochemically induced growth of aluminum oxide in a bath of sulfuric or phosphoric acids. *Spray pyrolysis* involves chemical reactions at the surface of a heated substrate. Increasingly transparent conducting coatings of tin oxide, bismuth-manganese alloy or indium tin oxide (ITO) 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 in many applications. The process was originally developed for aluminum and zirconium oxide but now extends to a wide range of glasses including silicates and phosphates, and has recently been applied to complex ferroelectrics such as BT (barium titanate), PZT (lead zirconate titanate) and PLZT (lead lanthanum zirconium titanate). Sol-gel coatings enjoy a high compositional flexibility and provide 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. Problems still exist related to inherent porosity and frequently insufficient adhesion of such coatings.

Thin coatings produced by *chemical vapor deposition (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%) microwave plasma. Much activity is currently devoted to the improvement of the thickness and the crystallographic perfection of diamond thin films in Japan and the United States. 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 (LEO) spacecraft 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 simplest vacuum technique. The materials to be deposited on a substrate are melted and vaporized either on a resistively heated tungsten, tantalum 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 and chemical purity, the excellent process control to generate 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 highly energetic ions from gas plasma or a separately exited ion beam, and to deposit 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 metalizing plastic ornaments and automotive components such as bumpers, for architectural glass, and for multi-layer holographic coatings on identification and credit cards to prevent forgeries.

Molecular beam epitaxy (MBE) permits deposition of very thin layers of ultra-pure elements and compounds in ultrahigh vacuum (10^{-8} Pa) at extremely low deposition rates (10^{-3} to 10^{-1} $\mu m\ min^{-1}$). Typically the elements to form the coating are heated in quasi-Knudsen effusion cells from which a ‘beam’ of material emerges. The evaporated elements, for example gallium and arsenic to deposit high-quality crystalline or precisely-doped gallium arsenide layers on silicon substrates condense on the substrate wafer surface. Since the mean free paths of the evaporated molecules or atom clusters are comparatively long they do not interact with each other until they reach the surface. In modern equipment, computer controlled shutters in front of the evaporation cells are used to control the rate of evaporation and hence the thickness and stoichiometry of the deposited layers. Most importantly, the slow deposition rates allow the films to be deposited epitaxially, and component layers are built up atom by atom with unmatched precision, crystallographic orientation and purity. During deposition, Reflection High Energy Electron Diffraction (RHEED) is frequently used to monitor the growth of the layers. Such close control allows the creation of structures to confine electrons in space forming quasi one-dimensional quantum wells and even quasi zero-dimensional quantum dots.

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 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 in 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 used widely to repair and resurface metallic surfaces but also, in recent years, to build up wear- and corrosion-resistant coatings, as well as chemical (CBCs) and thermal barrier coatings (TBCs) 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 bars and wires in reinforced concrete in bridge construction, coating of the inner surface of cylinders of internal combustion engines, and application of bioceramic coatings to hip and dental implants are just a short list of ever increasing fields of service of thermally sprayed coatings.

In recent years much research effort was expended on *kinetic* or *cold gas dynamic spraying* (CGDS). The decisive advantage of CGDS over competing conventional techniques is its low deposition temperature (gas temperature between 350 and 600 °C) in conjunction with high pressure of the carrier gas that imparts high kinetic energy to the solid powder particles. The CGDS technique was invented by Papyrin and co-workers in Russia (see for example Alkhimov *et al.*, 1994) and has been subject to intense industrial interest ever since (Voyer *et al.*, 2003; Gärtner *et al.*, 2006). The advantages of the technique include low temperature powder processing, phase preservation, very little oxidation of both coating and substrate, high coating hardness due to formation of a cold-worked microstructure, elimination of solidification stresses and hence the possibility of depositing thicker coatings, coatings with low defect density, low heat input into the substrate hence reduced cooling requirements, as well as reduced or even eliminated need for fuel gases, electrical heating and sample masking. However, there are still some noticeable disadvantages including high gas flow rates of costly gases such as helium, limitation of coating materials to ductile metallic powders, and the fact that the technology is still mainly in its R&D stage with little coating performance and history data. Notwithstanding the materials limitations, attempts have been reported in the literature to deposit ceramic coatings by CGDS. In particular, titania for photocatalytic application was deposited by CGDS onto stainless steel (Li and Li, 2003; Li *et al.*, 2004) and polymeric materials (Burlacov *et al.*, 2007).

Promising developments are under way such as spray systems that combine kinetic with thermal spraying (van Steenkiste and Fuller, 2004). For example, two particle populations are injected simultaneously into a de Laval-type nozzle one of which is thermally softened and the other is not. This can be achieved by using a mixture of small and larger particles of the same material whereby the smaller particles will melt or thermally soften at a main gas temperature that is insufficient to soften the larger particles. Also, particles with different morphologies can be injected: irregularly shaped particles will reside longer in the hot gas stream thus being more easily softened than spherical particles that offer the gas stream less resistance and hence leave the hot region faster. Alternatively, different material combinations can be used such as aluminum and copper, or aluminum and silicon carbide.

Dynamic deposition at even lower temperature (room temperature) can be successfully used to lay down thin (1–10 μm) or thick (100–100 μm), dense (> 95%) and well-adhering (20–50 MPa) ceramic coatings (alumina, yttria, titania, PZT, AlN, MgB_2) on a variety of substrates including stainless steel, glass, silicon and polymers. The process is called aerosol deposition (AD) that relies on so-called room temperature impact consolidation (RTIC). An aerosol flow consisting of a carrier gas (nitrogen, helium) and a fine ceramic powder (0.1–1 μm) is ejected through a micro-orifice nozzle to acquire a velocity of up to $500\,m\,s^{-1}$, and made to impact onto the substrate in an evacuated deposition chamber (Akedo and Lebedev, 1999; Akedo *et al.*, 2005; Akedo, 2006). The exact physics behind the process, however, has not been elucidated in much detail to date. While the temperature increase gained during impact is too low to cause widespread sintering in contrast to shock consolidation, fracture and plastic deformation of the ceramic powder particles may play a role. Also, generation by impact of clean and active surfaces that subsequently promote chemical reactions between the coating and substrate materials can be envisaged (Akedo, 2006).

In conclusion, advanced materials coatings are becoming more and more popular with materials engineers. The equipment, ease of application of coatings to complex surfaces, and the availability of tailored feedstock materials together with sophisticated process control and modern coating characterization techniques make novel surface coatings increasingly attractive. Thus it has been said that coatings technology will be the materials technology of the twentyfirst 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 metals surfaces by flame spraying to enhance corrosion performance (Schoop and Guenther, 1917). The field developed quickly and spread to other countries, and in 1926 a comprehensive book was published by T.H. Turner and N.F. Budgen on *Metal Spraying* (Turner and Budgen, 1926). This book was re-edited in 1963 under the title *Metal Spraying and the Flame Deposition of Ceramics and Plastics* to reflect the shift from metals to other materials.

Figure 1.2 gives an impression of the pace of development of the thermal spray technology (Smith, 2004). It illustrates those applications that have been either pushed or made possible by the technological progress (Heimann, 1991b) while highlighting 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 developed and applied by Union Carbide Corp. found a receptive market in the aerospace industry, and a large proportion of the subsequent technological growth was due to plasma-sprayed TBCs based on stabilized zirconia. The second growth spurt shown in the figure occurred in the 1980s by the invention of the VPS/LPPS and the Jet Kote™/HVOF techniques as well as the high temperature coatings for aerospace gas turbines associated therewith (Figure 1.3, Sivakumar and Mordike, 1989).

Future developments, undoubtedly highlighted by a further increase in the rate of technological innovation, will include improved on-line real-time feedback control with close-loop strategies, intelligent statistical process control (iSPC), 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. A recent summary of the development of DC plasma spraying (Fauchais *et al.*, 2006) indicates four main focus points of current developments:

- process on-line control requiring correlation of particle in-flight characteristic as well as substrate and coating temperatures to thermo-mechanical and other in-service coating properties;
- study of arc root fluctuations and their causes by experiments and 3D modeling, and relating them to structure and properties of coatings;
- study of splat formation and layering mechanisms and their effect on the properties of splat-substrate and splat-splat interfaces;
- development of novel spray techniques to produce nano-structured coatings, in particular using suspension and solution plasma spraying.

In the last three to four decades there has been increasing interest in coatings by the military and the commercial sector that led to a wealth of information. Journals totally dedicated to thermal spraying exist, for example the *Journal of Thermal Spray Technology*, but also journals devoted to the entire realm of surface engineering, for

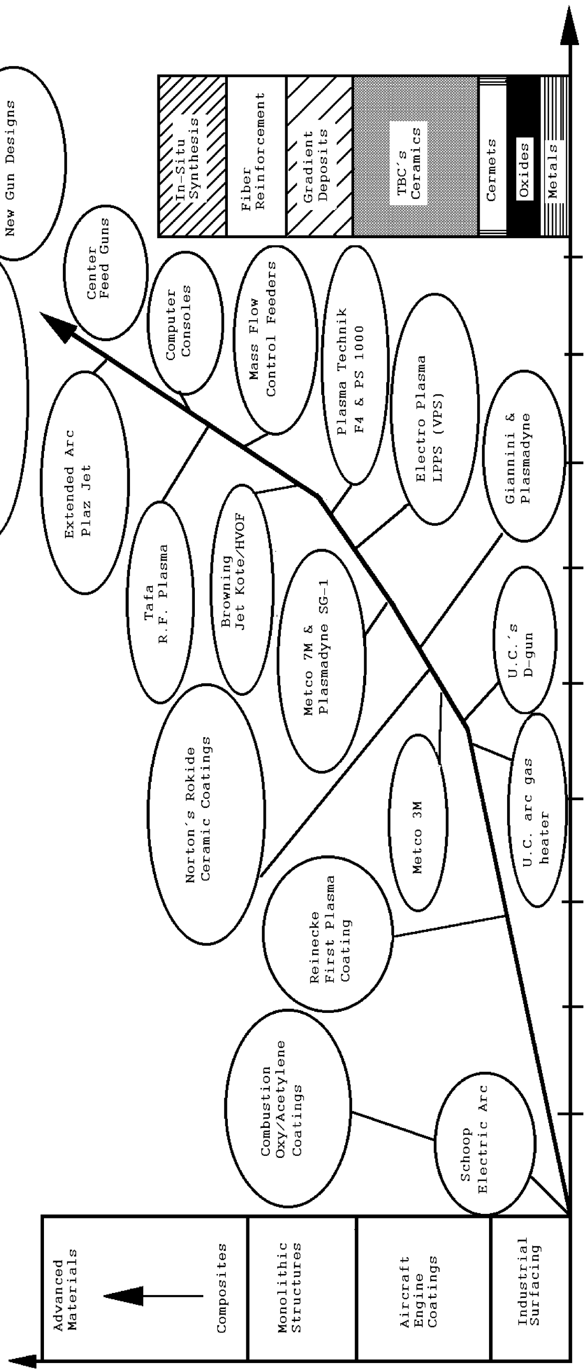

Figure 1.2 Milestones of thermal spray technology growth (Smith, 2004).

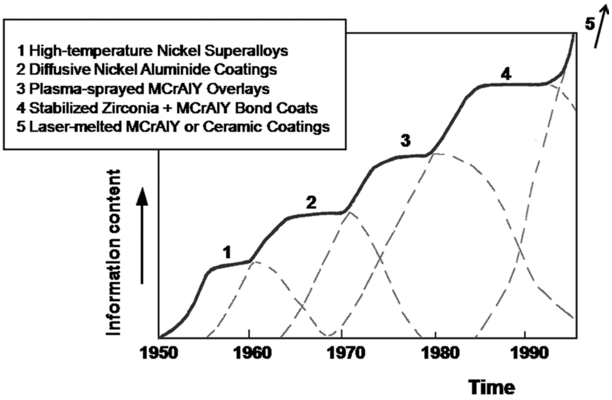

Figure 1.3 Evolution of high-temperature coatings for aerospace gas turbines (Sivakumar and Mordike, 1989).

example *Surface and Coating Technology, Thin Solid Films, Surface Technology, Acta Materialia, Materials Science and Engineering, Advanced Materials* and *Journal of Materials Science*. Biannual national and triannual international conferences present ongoing worldwide university and industry research and development efforts in a wide variety of thermal spray processes. Several monographs and handbooks dealing with plasma spraying are available, for example Matejka and Benko 1989, Barthelmess *et al.* 1992, Wachtman and Haber 1993, ASM Handbook 1994, Pawlowski 1995, Stern 1996, Davis 2004, d'Agostino *et al.* 2007 and more.

Activities are well under way to develop expert systems that integrate exhaustive databases with expert knowledge and practical experiences, being supported by ever more sophisticated 3D modeling and numerical simulation of the complex interaction of plasma, particles and substrate. 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 as to how and where the coatings are being used. These databases provide detailed information on over 1300 thermal spray applications and contain a listing of international suppliers. The materials covered are categorized into 12 groups including iron-based materials, nickel-based materials, cobalt-based materials and nonferrous metallic-based materials (Longo *et al.*, 1994).

To unravel the inherent complexity of the deposition process, and the influence of plasma parameters on coating properties traditionally a statistical design of experimentation (SDE) approach is used. However, insight into the complex interrelation of the parameters, intermediate sub-processes and their corresponding mechanisms is largely missing. Hence a concerted, integrated interdisciplinary approach is required that has been found in the development of so-called *process maps* (Sampath *et al.*, 2003). Details of a case study of Mo coatings on steel can be found in Chapter 11.1.4.

Process simulation plays an increasingly important role in estimating the interdependence of spraying parameters and desired coating properties (Knotek and Schnaut, 1993; Nylén *et al.*, 1999; Ahmed and Bergman, 2000; Sevostianov and Kachanov, 2000; Feng *et al.*, 2002; Williamson *et al.*, 2002; Ghafouri-Azar *et al.*, 2003;

Raessi and Mostaghimi, 2005) as well as ever more complex modeling and numerical simulation of the generation of plasma and its interaction with materials immersed in the plasma jet (see Chapter 6).

The main research and development activities today center around:

- improving powder feedstocks, spray application equipment, and process control through Statistical Design of Experiments (SDE), intelligent Statistical Process Control (iSPC), and Quality Function Deployment (QFD) techniques (see Chapter 11);
- designing new control devices, on-line real-time feedback looping, mass flow controllers, powder metering equipment, manipulators and robots (Borbeck, 1983; Barbezat, 2002, 2005);
- development of novel spray technologies, e.g. reactive plasma spraying (Pfender, 1999; see Chapter 7.1.2.2), suspension plasma spraying (SPS; Gitzhofer *et al.*, 1997; Müller, 2001; Fauchais *et al.*, 2005; see Chapter 8.2.2), thermal plasma chemical vapor deposition (TPCVD; Zhu *et al.*, 1991; Kolman *et al.*, 1998; Müller, 2001; see Chapter 8.2.2), reactive laser plasma coating (Schaaf *et al.*, 2005), high velocity pulsed plasma spraying (HVPPS; Witherspoon *et al.*, 2002), high velocity suspension flame spraying (HVSFS; Killinger *et al.*, 2006; Gadow *et al.*, 2006) and electromagnetically accelerated plasma spraying (EMAPS, Kitamura *et al.,* 2003; Usuba and Heimann, 2006; see Chapter 8.4);
- design and commissioning of new plasmatrons such as three-cathode systems (Triplex I and II; Sulzer Metco, Zierhut *et al.*, 1998), plasmatrons with axial injection (Axial III; Northwest Mettech Corp., Moreau *et al.*, 1995), plasmatrons with rotating heads for coating internal surfaces (Sulzer Metco, Barbezat, 2002), and r.f. plasmatrons for high power levels up to 200 kW (Tekna Corp., Boulos, 1997);
- effective innovation and technology transfer from research organizations to small and medium-sized enterprises (SMEs) (Riesenhuber, 1989);
- development of data bases and expert systems (Kern *et al.*, 1990) as well as process maps (Sampath *et al.*, 2003).

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 in industry are:

- creep strength;
- fatigue strength;
- flexural strength;
- ductility;

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

Typical ceramic properties are:

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

The combination of these properties yields a superior 'composite' material. However, several aspects must be carefully controlled, such as the difference in the coefficients of thermal expansion of metal and ceramic which leads to undesirable stresses at the interface substrate/coating that impose the risk of cracking, spalling, and eventually delamination of the coating. Also, the generally high porosity of plasma-sprayed ceramics has to be dealt with, unless it is a desired property, by infiltrating the coating with another material, hot isostatically pressing, or by laser densification or other techniques (see Chapter 8.1.3). The low fracture toughness of the ceramic is also point 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 are an ever increasing number of technical applications of plasma-sprayed metal and ceramic coatings. Many of such applications resulted from the demand of 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. It is not possible to cover here all present and potential applications of thermally sprayed coatings. The listing 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 (Pawlowski, 1995):

- problem identification;
- specification of coating properties;
- suggestion of solutions including selection of materials to be sprayed, equipment and technique used and so on;

- application of coating;
- 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;
- coating of the inner surface of cylinders of internal combustion engines to facilitate the move from steel of light metal motor blocks;
- resurfacing of worn equipment, for example in railway transportation application, ship building and maintenance and mining tools and equipment;
- superalloy coatings for aerospace gas turbine vanes and shrouds to prevent hot gas erosion and corrosion;
- ceramic membranes for osmotic filtering and ultrafiltration;
- biomedical coatings for dental and bone implants with biocompatible and, in particular bioconductive properties based on hydroxyapatite and tricalcium phosphate, respectively;
- stabilized zirconia electrolyte and electrocatalytically active compound coatings for solid oxide fuel cells (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;
- photocatalytically active coatings for UV-activated cleaning devices for domestic and industrial waste water;
- high grip/high friction coatings for space-bound applications;
- 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 the case studies presented in Chapters 7 to 9.

References

R. d'Agostino, P. Favia, Y. Kawai, H. Ikegami, N. Sato, F. Arefi-Khonsari. *Advanced Plasma Technology.* Wiley-VCH: Berlin. ISBN: 3-527-40591-7. 2007.

I. Ahmed, T.L. Bergman, *J. Thermal Spray Technol.*, 2000, **9** (2), 215.

J. Akedo, *J. Am. Ceram. Soc.*, 2006, **89** (6), 1834.

J. Akedo, M. Lebedev, *Jpn. J. Appl. Phys.*, 1999, **38**, 5397.

J. Akedo, M. Lebedev, H. Sato, J. Park, *Jpn. J. Appl. Phys.*, 2005, **44**, 7072.

L.S. Alf, *Quality Improvement Using Statistical Process Control*, HBJ Publishers: New York, 1988.

P. Alkhimov, A.N. Papyrin, V.P. Dosarev, N.J. Nesterovich, M.M. Shuspanov, US Patent 5,302,414 (April 12, 1994).

ASM Handbook. Vol 05, *Surface Engineering*, ASM International: Materials Park, OH. ISBN: 0-87170-384-X. 1994.

G. Barbezat, *Automot. Technol.*, 2002, **2**, 47.

G. Barbezat, *Application of thermal spraying in automotive industry*, Proc. 2ièmes RIPT, Lille, France, 1–2 Décembre 2005, 231.

H. Barthelmess, H. Becker, U. Klimpel, *Plasmaspritzen*, DS Informationssysteme für die Schweisstechnik, Fachbibliothek Schweisstechnik, 53 series, ISBN: 3-871-55650-5. 1992.

K.D. Borbeck, in: Proc.10th ITSC, Essen 1983, DVS 80, 99.

M.I. Boulos, *J. High Temp. Mater. Process.*, 1997, **1**, 17.

R.F. Bunshaw, *Deposition Technologies for Thin Films and Coatings*, Noyes Publications, Park Ridge, N.J., 1982.

I. Burlacov, J. Jirkovsky, L. Kavan, R. Ballhorn, R.B. Heimann, *J. Photochem., Photobiol. A*, 2007, **187** (2–3), 285.

K. Chan, J.B. Wachtman, *Ceramic Industry*, 1987, **129**, 24.

J.R. Davis (ed.), *Handbook of Thermal Spray Technology*, ASM International: Materials Park, OH. ISBN: 9-780-87170-795-6. 2004.

P. Fauchais, V. Rat, C. Delbos, J.F. Coudert, T. Chartier, LK. Bianchi, *IEEE Trans. Plasma Sci.*, 2005, **33** (2), 920.

P. Fauchais, G. Montavon, M. Vardelle, *J. Cedelle Surf. Coat. Technol.*, 2006, **201** 1908.

Z.G. Feng, M. Domaszewski, G. Montavon, C. Coddet, *J. Thermal Spray Technol.*, 2002, **11** (1), 62.

R. Gadow, F. Kern, A. Killinger, *Mater. Sci. Eng. B.*, doi:10.1016/j.mseb.2007.09.066.

F. Gärtner, T. Stoltenhoff, T. Schmidt, H. Kreye, *J. Thermal Spray Technol.*, 2006, **15** (2), 223.

R. Ghafouri-Azar, J. Mostaghimi, S. Chandra, M. Charmchi, *J. Thermal Spray Technol.*, 2003, **12** (1), 53.

F. Gitzhofer, E. Bouyer, M.I. Boulos, *Suspension Plasma Spray*, US Patent 5,609,921, 1997.

Gorham Advanced Materials Institute, *Thermal Spray Coatings*, Gorham, Maine, USA, 1990.

Gorham Advanced Materials Institute, *Thermal S pray Coatings*, Gorham, Maine, USA, 1999.

R.B. Heimann, *Process. Adv. Mat.* 1991a, **1**, 181.

R.B. Heimann, *Am. Ceram. Soc. Bull.*, 1991b, **70**, 1120.

L.L. Hench, *J. Am. Ceram. Soc.* 1991, **74**, 1487.

H. Henke, D. Adam, A. Köhler, R.B. Heimann, *Wear*, 2004, **256**, 81.

H. Kern, M. Fathi-Torbaghan, M. Stracke, in: Proc. TS'90, Essen 1990, DVS 130, 247.

A. Killinger, M. Kuhn, R. Gadow, *Surf. Coat. Technol.*, 2006, **201** (5), 1922.

J. Kitamura, S. Usuba, Y. Kakudate, H. Yokoi, K. Yamamoto, A. Tanaka, S. Fujiwara, *J. Thermal Spray Technol.*, 2003, **12** (1), 70.

O. Knotek, U. Schnaut, in: Proc.TS'93, Aachen 1993, DVS 152, 138.

D. Kolman, J. Heberlein, E. Pfender, *Plasma Chem. Plasma Process.*, 1998, **18** (1), 73.

C. J. Li, W.Y. Li, *Surf. Coat. Technol.*, 2003, **167**, 278.

C.J. Li, G.J. Yang, X.C. Huang, W.Y. Li, A. Ohmori, in: E. Lugscheider (ed.), Proc. Intern. Thermal Spray Conf., ITSC 2004, Osaka, Japan, DVS-Verlag, p. 315.

F.H. Longo, H. Herman, K. Kowalski, *The Thermal Spray Source Program*, MS Card. CRC Press, London, ISBN: 0-849-38639-X. 1994.

R. Maier (ed.), *Technische Keramik als Innovationsgrundlage für die Produkt- und Technologie-Entwicklung in NRW.* Ministerium für Wirtschaft, Mittelstand und Technologie des Landes Nordrhein-Westfalen, December 1991, p. 108.

D. Matejka, B. Benko, *Plasma Spraying of Metallic and Ceramic Materials*, Wiley: Chichester. ISBN: 0-471-91876-8. 1989.

C. Moreau, P. Gougeon, A. Burgess, D. Ross, in: S. Sampath, C.C. Berndt (eds.), *Advances in Thermal Spray: Science and Technology*, ASM Int., Materials Park, OH, USA, 1995, 41.

M. Müller, *Entwicklung elektrokatalytischer Oxidschichten mit kontrollierter Struktur und Dotierung aus flüssigen Prekursoren mittels thermischer Hochfrequenzplasmen*, Unpublished Ph.D. Thesis, Technische Universität Bergakademie Freiberg, Germany, June 2001.

M. Müller, E. Bouyer, M. v.Bradke, D.W. Branston, R.B. Heimann, R. Henne, G. Lins, G. Schiller, *Mater.-wiss.u.Werkstofftech.*, 2002, **33**, 322.

P. Nylén, J. Wigren, L. Pejryd, M.-O. Hansson, *J. Thermal Spray Technol.*, 1999, **8** (3), 393.

L. Pawlowski, *The Science and Engineering of Thermal Spray Coatings.* Wiley: Chichester, New York, Brisbane, Toronto, Singapore. 1995.

E. Pfender, *Plasma Chem. Plasma Proc.*, 1999, **19** (1), 1.

M. Raessi, J. Mostaghimi, *Numer. Heat Transfer B*, 2005, **47**, 1.

J. Read, ITSC, Keynote address, China Intern. Thermal Spray Conf., Dalian, China, Sept 22–25, 2003.

H. Reh, *Keram. Zeitschrift*, 1989, **41** (3), 176.

H. Riesenhuber, *Vakuum-Technik*, 1989, **38** (5/6), 119.

S. Sampath, X. Jiang, A. Kulkarni, J. Matejicek, D.L. Gilmore, R.A. Neiser, *Mater. Sci. Eng. A*, 2003, **348**, 54.

M. Sayer, *Can. Ceramics Quarterly*, 1990, **59** (1), 21.

P. Schaaf, M. Kahle, E. Carpene, *Surf. Coat. Technol.*, 2005, **200**, 608.

M.U. Schoop, H. Guenther, *Das Schoopsche Metallspritz-Verfahren*, Franckh-Verlag: Stuttgart, Germany, 1917.

I. Sevostianov, M. Kachanov, *Acta Mater.*, 2000, **48**, 1361.

R. Sivakumar, B.L. Mordike, *Surf. Coat. Technol.*, 1989, **37**, 139.

R.W. Smith, in: *Handbook of Thermal Spray Technology*, 06994G, ASM International: Materials Park, OH, 2004.

K.H. Stern (ed.), *Metallurgical and Ceramic Protective Coatings*, Chapman & Hall: London. ISBN: 0-421-54440-7. 1996.

T.H. Turner, N.E. Budgen, *Metal Spraying*, Charles Griffin: London, 1926.

S. Usuba, R.B. Heimann, *J. Thermal Spray Technol.*, 2006, **15** (3), 356.

T.H. van Steenkiste, B.K. Fuller, US Patent 7,108,893 2004.

J. Voyer, T. Stoltenhoff, H. Kreye, C. Moreau, B. Marple (eds.), *Thermal Spray 2003: Advancing the Science & Applying the Technology*, ASM International, Materials Park, OH, USA, 2003, p. 71.

J.B. Wachtman, R.A. Haber (eds.), *Ceramic Films and Coatings*, Noyes Publications: Park Ridge, N.J. 1993.

R.L. Williamson, J.R. Fincke, C.H. Chang, *J. Thermal Spray Technol.*, 2002, **11** (1), 107.

F.D. Witherspoon, D.W. Massey, R.W. Kincaid, G.C. Whichard, T.A. Mozhi, *J. Thermal Spray Technol.*, 2002, **11** (1), 119.

M. Woydt, N. Kelling, M. Buchmann, *Mat.-wiss.u.Werkstofftech.*, 2004, **35** (10/11), 824.

H. Zhu, Y.C. Lau, E. Pfender, *J. Appl. Phys.*, 1991, **69** (5), 3404.

J. Zierhut, P. Haslbeck, K.D. Landes, G. Barbezat, M. Müller, M. Schütz, in: C. Coddet (ed.), *Thermal Spray: Meeting the Challenges of the 21st Century*, ASM Int., Materials Park, OH, USA, 1998, 1375.