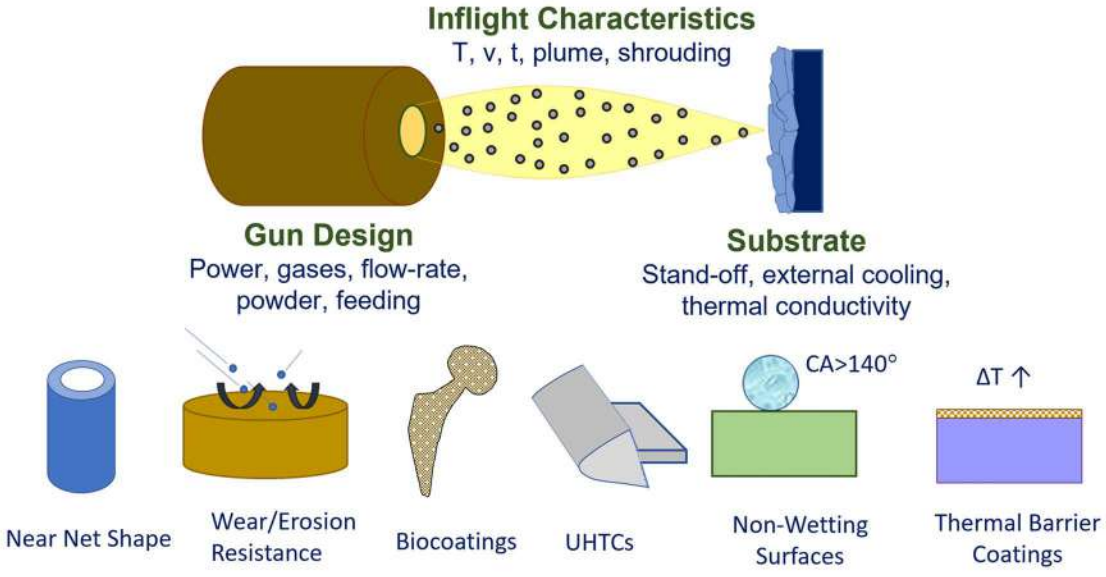
Fundamentals of Thermal Spraying



Edited by
Ariharan S, Rubia Hassan, Alok Bhadauria, Ashutosh Tiwari, Ritik Tandon, Anup Kumar Keshri and Kantesh Balani

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Fundamentals of Thermal Spraying

This book discusses the concepts and uses of thermal spraying including starting powder, spraying parameters, diagnostics, coating deposition, evolved microstructure and resulting properties complemented with several case studies to associate the learnings with applied concepts. The major parts of the instrumentation, the spraying gun, which is the fundamental aspect of different thermal spraying conditions are also discussed. Solved examples, numerical problems and descriptive questions are included for self-assessment at the end of every chapter.

The book:

- Discusses all aspects from starting powder, spraying parameters, diagnostics and coating deposition;
- Explores schematics to highlight the conceptual notes;
- Includes multiple case studies from domains including aerospace, biomedical, manufacturing, wettability and others to highlight the practical application of thermally sprayed coatings;
- Covers classification of thermal spray techniques; and
- Contains solved examples, numerical problems and descriptive questions for self-assessment.

This book is aimed at senior undergraduates and graduates in materials science and engineering.



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Foreword

It is my pleasure to write the foreword of the book *Fundamentals of Thermal Spraying*, edited by Ariharan S, Rubia Hassan, Alok Bhadauria, Ashutosh Tiwari, Ritik Tandon, Anup Kumar Keshri and Kantesh Balani.

After reading this book, I can say that this is one among the most comprehensive presentations in this field, especially for undergraduate and postgraduate students as a perfect textbook. The book contains 11 chapters and covers all the fundamentals of thermal spraying, starting from powder characteristics to fabrication of the final part. The book starts its journey from the historical perspective of Schoop's patent, leads the reader to the need for surface coatings, takes effort in classifying the thermal spray techniques, and emphasizes myriad spraying parameters that affect the characteristics of the finally deposited coating. Various comparisons in terms of microstructure, performance of coatings, process parameters and so forth provide a good perspective of the differences between various thermal spraying techniques. The description of gun designs with plasma stability, gas parameters, powder feeding and injection, along with the science behind coating formation starting with single splat formation, is commendable. The details of powder characterization, powder production and powder feeders with its working principle highlight the rigor authors have taken to provide right understanding to readers. The aspects of Rayleigh criterion to heat transfer and splat layering and deposition to emanate with final microstructure is also very lucidly described. Authors contribute on the various aspects of coating reliability, providing assessment of adhesion tests and data analysis via Weibull distribution. The aspect of process diagnostics in providing thermal and kinetic history of the in-flight particles is also a key contribution of this book. The emerging aspect of machine learning is also a good addition. The extension of thermal spraying towards achieving freestanding and near-net shaped structures is also emphasized by the authors. Several selected case studies, presented by authors on biomaterials, corrosion resistance, thermal barrier coating and so forth are also noteworthy, as they provide a direct use of thermal spraying in various fields.

The book becomes more special because the authors have taken extra effort to present ideas with schematics and have provided solved numerical problems and questions for self-analysis.

In short, I will give my highest recommendation to this book as a textbook for undergraduate and postgraduate students. This book will also serve as a firsthand reference even for experienced researchers, developers and engineers working in the area of thermal spraying.

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Preface

This textbook is a comprehensive version of a standard thermal spraying textbook, covering almost all the aspects of thermal spraying in brief and simple terms which makes it suitable for the curriculum at the undergraduate level. This compilation is produced with the intention of providing a background for thermal spray technology, which comprises a collection of coating techniques providing protection and/or improved performance to the substrate. Through this book, students will gain confidence for further reading beyond this text to gain expertise in the field.

Of the numerous books available on thermal spraying, most are designed for graduate level and as reference books providing access to a huge yet complicated volume of literature in the field. The current text aims at providing an understanding of the fundamentals of thermal spraying encompassing basic concepts from starting powder to final coated surface. The incorporation of intelligible schematics and inclusion of numerical problems throughout different sections will assist in comprehending the practical aspects of these concepts. In the process of covering all the major aspects of the field and simultaneously designing it to be simple and easily comprehensible, the authors confronted the need to keep the topics concise.

Eleven chapters are presented in this book. Chapter 1 is dedicated to different techniques for thermal spraying and starts with information about the evolution of thermal spraying processes. The history of thermal spraying began with Schoop's patent on flame spraying; later, Schoop also developed the electric arc–spraying process. A comparison of thermal spraying technology is made with other coating techniques, and thermal spraying provides an added benefit of depositing almost any material on practically any substrate to cover a wide range of applications. Further, the need for coating the surfaces of components in engineering applications is highlighted.

Chapter 2 is devoted to surface coatings, discussing the concept of surface and requirement of surface modification through different approaches of which coating is superior to the other techniques. It discusses the reasons for surface failure through wear, erosion, corrosion, high temperature oxidation and so on, and consecutively builds up the platform for utilizing different surface modifications to deal with various issues. Apart from serving as a protective shield against the surface damage of the substrate material, coatings can be applied to induce electrical insulation or electrical conductivity in the material and can also be utilized to impart an aesthetic look for decorative purposes. Of all the surface modification approaches, thermal spraying appears to be most advantageous owing to its versatility in terms of the materials deposited, as well as in terms of the properties of the coatings obtained.

Chapter 3 discusses in detail various thermal spraying techniques, highlighting pros and cons of each technique. The major classes of thermal spraying

techniques, classified on the basis of heating source, include combustion spraying, electric arc spraying and plasma spraying. The cold-spraying process, which uses kinetic energy to accelerate the powder particles to supersonic velocities using convergent-divergent nozzles, has also been given a due position in this classification and is utilized in various important applications like medical and aerospace technologies.

Chapter 4 is dedicated to a discussion on spraying parameters. Each and every parameter involved in thermal spraying has an effect on the final deposited coating. In-flight condition of powder particles during spraying, expressed in terms of temperature and kinetic velocity, depends on powder characteristics like powder particle size and shape, powder feed rate, nature of carrier gas, enthalpy of plasma forming gases (for plasma spraying), distance between powder-spray gun and the substrate, and the preparation of substrate material prior to deposition. Presence of any undesirable impurity on the substrate could spoil all the efforts taken to optimize the sparing parameters and may compromise the integrity of the coating. Minimum wastage of powder and maximum deposition as coating needs to avoid entrapment of oxide/un-melted particles in the deposited coating.

Chapter 5 deals with the design of spray guns because it strongly influences spraying parameters like feed rate and particle velocity and temperature that determine the quality of the deposited coating. In cold spraying, an ultra-high velocity, required for deposition of particles as coating through plastic deformation, is attained using a special gun design with a converging and diverging type nozzle. On the other hand, spray guns for combustion-based techniques are relatively simple. Similarly, the gun design changes for other spraying techniques.

Chapter 6 discusses the powder characterization and powder synthesis. The feed material in thermal spray processes is usually in powder form, and the powder characteristics are reflected in the nature and quality of the coating. Thus, different powder morphology and powder size distribution induce different in-flight velocity and thermal characteristics. Different particle sizing techniques and associated equivalent diameters of particles are illustrated in this chapter. A spherical powder morphology helps in maintaining the flowability and regular feed rate. However, different synthesis techniques produce powders of different morphology and sizes, and modification may be required before feeding the powder in the thermal spray process. Modification of particle shape through techniques like spheroidization and particle size through mechanical reduction and consolidation are dealt with in the chapter.

Chapter 7 presents coating development through the formation of splats and layering of successive splats. Splat formation from incoming particles is dictated by the state of the particle (molten, partially molten or solid), heat transfer between the particle and the substrate, particle velocity and the preheating of the substrate. The mechanisms involved during its formation and successive deposition are discussed in the chapter. An interaction of incoming particles with the substrate in the making of splats and also between the successively depositing splats is associated with heat transfer, metallurgical bonding and mechanical

integration. The final microstructure of the coating and its densification determine the functionality of the coating.

In Chapter 8, special attention is directed towards the testing of thermal spray coatings. The methods of coating characterization and preparation required prior to the standard test methods are discussed. Microstructural evolution, phase identification and phase quantification, estimation of basic physical, mechanical and thermal properties are also covered. The microstructure of the thermal spray coating, porosity and presence of any oxide or un-melted phase govern the properties and performance of the coating. Accordingly, characterization of microstructure and evaluation of performance through non-destructive or destructive testing is necessitated. This chapter discusses various approaches of porosity calculation in the microstructure, phase evaluation, mechanical property determination including hardness, fracture toughness and adhesive strength; thermal properties like thermal conductivity and thermal shock resistance; and wear properties under different conditions like fretting, abrasion, surface fatigue and erosion.

Chapter 9 provides insight to process diagnostics and online monitoring and control. Knowing that the kinetic velocity and temperature of particles are governing factors in thermal spraying, it becomes essential to measure and control these parameters for efficient deposition. In-flight particle parameters and their effect on microstructure, plume profiling, particle in-flight temperature, velocity distributions and their measurements using different diagnostic systems, and the limitations in the monitoring of in-flight particle in order to achieve constant repeatability, reproducibility and reliability is discussed in this chapter.

Chapter 10 engages the reader in development of nanostructured and near-net shapes of coatings. A wide variety of simple and complex configurations of coatings can be prepared through near-net shape processing. Bulk nanostructured coatings can also be engineered via thermal spraying. Due to high temperatures, almost all materials can be melted, which makes these processes suitable for spraying of near-net shape with specific thickness and geometries at different parts of the complex shapes. The development of a freestanding nanostructured near-net shape lies in the fact that nanostructure is retained without any significant alteration of grain size.

Chapter 11 covers some of few case studies on biomedical coatings, thermal barrier coatings, alternate chrome plating techniques, and corrosion-resistant and ultra-high-temperature coatings engineered through thermal spraying. These case studies facilitate the reader learning the need for thermal spraying in these important applications.

This book is a result of collective effort from all the authors, but the genesis of this project was realized after an enthusiastic involvement of Dr. Ariharan S, Dr. Rubia Hassan, Prof. Anup Kumar Keshri, Prof. Ashutosh Tiwari, Dr. Alok Bhadauria, Mr. Ritik Tandon, and Prof. Kantesh Balani. The idea was formed when Prof. Balani taught the course "MSE634: Fundamentals of Thermal Spraying" at IIT Kanpur in fall 2013 and then again in fall 2017 and felt the need to create a textbook. All the authors have strongly contributed to tailoring the writing to suit an undergraduate perspective by creating schematics, self-analysis questions

and numerical problems where feasible. Authors AT and KB acknowledge *TARE* (TAR/2018/000310, Science and Engineering Research Board, Department of Science and Technology, Govt. of India). KB acknowledges the *Swarnajayanti Fellowship* (DST/SJF/ETA-02–2016–17, Department of Science and Technology, Govt. of India); *Indian Space Research Organization* (Vikram Sarabhai Space Centre, Space Technology Cell at IIT Kanpur); the Ministry of Education (erstwhile Ministry of Human Resources and Development), Govt. of India; and the *Yadupati Singhania Memorial Chair* of IIT Kanpur. AS acknowledges the *National Post-doctoral Fellowship*, and RH acknowledges the *Prime Minister Research Fellowship*. Authors extend a special gratitude to Prof. Arvind Agarwal for writing the foreword of this book. We acknowledge our host institutions including IIT Kanpur, IIT Patna, REC Banda, and Anod Plasma Spray Limited for facilitating research and encouragement in our respective departments.

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Abbreviations

AIP-PVD	Arc ion plating physical vapor deposition
Al_2O_3	Alumina
APS	Air plasma spraying
Ar	Argon
ASPS	Axial suspension plasma spraying
BeO	Beryllium oxide
BET	Brunauer-Emmett-Teller
CA	Contact angle
CAH	Contact angle hysteresis
C/C	Carbon/carbon
CCD	Central composite design
CeO_2	Cerium oxide
CFD	Computational fluid dynamics
CNT	Carbon nanotube
COC	Ceramic-on-ceramic
COP	Ceramic-on-polyethylene
CS	Critical speed
CTE	Coefficient of thermal expansion
CVD	Chemical vapor deposition
DC-TRAP	DC-triple plasma atomization process
D-gun	Detonation gun
Dj	Diamond jet
DOE	Design of experiments
EB-PVD	Electron beam physical vapor deposition
EDS	Energy dispersive spectroscopy
EIGA	Electrode induction gas atomization
EMI	Electromagnetic interference
EPMA	Electron probe micro-analyzer
FWHM	Full width half maximum
GAP	Gas atomization process
H_2	Hydrogen
HAp	Hydroxyapatite
HCF	Hip contact forces
HCPEB	High-current pulsed electron beam
He	Helium
HIP	Hot isostatic pressing
HPCS	High-pressure cold spraying
HPPS	High-pressure plasma spraying
HVAF	High-velocity air fuel
HVOF	High-velocity oxy-fuel
Hyperpoc	Hydrogen pressure reducing powder coating

ICDD	International crystal diffraction data
ICIC	Inflammatory cell-induced corrosion
IGA	Inert gas atomization
IPP	In-flight particle pyrometer
IPS	Inert gas plasma spraying
LCS	Low-carbon steel
LDH	Layered double hydroxides
LFA	Low-friction arthroplasty
LPCS	Low-pressure cold spraying
LPPS	Low-pressure plasma system
LVDT	Linear variable differential transformer
MAC	Mechanically assisted corrosion
ML	Machine learning
MMC	Metal matrix composite
MOM	Metal-on-metal
MOP	Metal-on-polyethylene
MSR	Mechanical size reduction
N_2	Nitrogen
N.A.	Numerical aperture
NC	Nanostructured coating
NDT	Non-destructive testing
NIR	Near infrared
OA	Osteoarthritis
OCP	Open circuit potential
ODS	Oxide-dispersion strengthened
OR	Outside range
PCA	Process control agent
PLD	Pulsed laser deposition
PREP	Plasma rotating electrode process
PSD	Particle size distribution
PVD	Physical vapor deposition
PWT	Plasma wind tunnel
RA	Rheumatoid arthritis
REO	Rare earth oxides
REP	Rotating electrode process
RFI	Radiofrequency interference
RF-IPAP	RF-induction plasma atomization process
RRR	Repeatability, reproducibility and reliability
SCP	Spray conversion processing
SDC	Spray and deposit control
SEM	Scanning electron microscope
SHS	Self-propagating high-temperature synthesis
SMAT	Surface mechanical attrition treatment
SOFC	Solid oxide fuel cells
SPPS	Suspension/solution precursor plasma spraying

SPS	Spark plasma sintering, suspension plasma spray
SS	Stainless steel
SVM	Support vector machine
T	Temperature
TBC	Thermal barrier coating
TEM	Transmission electron microscopy
THA	Total hip arthroplasty
THR	Total hip replacement
TKA	Total knee arthroplasty
TMAH	Tetramethylammonium hydroxide
TPS	Thermal protection system
TSC	Thermal-sprayed coating
TSR	Thermal shock resistance
UHMWPE	Ultra-high-molecular-weight polyethylene
UHTC	Ultra-high-temperature ceramics
VIGA	Vacuum inert gas atomization
VOC	Volatile organic compound
VPS	Vacuum plasma spraying
WC	Tungsten carbide
WCA	Water contact angle
XRD	X-ray diffraction
YSZ	Yttria-stabilized zirconia
ZrO_2	Zirconia



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Symbols

A	Cross-sectional area, projected area, empirical constant
a_c	Diagonal length of the indent
A_e	Exit area
A_i	Area of nozzle exit
A_t	Nozzle throat area
α	Linear expansion coefficient, thermal diffusivity
α_l	Mean thermal expansion coefficient
α_v	Fractional change in volume with temperature
B	Biot number
c	Half crack length, velocity of light
C_d	Drag coefficient
CI	Confidence interval
C_i	Volume fraction
c_i	Velocity of the liquid drop
C_p	Specific heat capacity
d	Sliding distance
D	Theoretical density, flattened particle diameter
d_0	Arithmetic mean
d_a	Projected area diameter
d_s	Surface diameter
d_v	Volume diameter
d_{32}	Sauter diameter
D_p	Particle diameter
δ	Resolution of the microscope, offset
E	Young's modulus
E_x	Electric field
$E(\lambda)$	Thermal flux
e	Electron charge
e_T	Dilatational strain
η	Fluid viscosity, arithmetic mean of experimental dataset, Poisson's ratio, transformation zone factor
F	Feret diameter, applied load
F_N	Applied load
F_T	Structure factor
g	Acceleration due to gravity
γ	Specific heat ratio, surface tension
H	Substrate thickness, hardness
h	Coefficient of heat transfer, coating thickness, droplet height, phase transformation zone
H_v	Vickers hardness
I	Solidification rate

I_c Index of crystallinity, crack length from the corner of the indentation
I_i^P Diffracted intensity
I_o Incident beam intensity
j_l Spherical Bessel function
K Sommerfeld number
k Wave number, thermal conductivity
k_B Boltzmann constant
K_{1c} Fracture toughness
L Length at temperature T, thickness of the specimen
L_c Critical load
L_f Enthalpy of fusion
LP Lorentz polarization factor
λ Wavelength of light, scaling parameter
M Mach number, Martin diameter
m Rate of mass flow of gas, Weibull modulus
m_e Mass of electron
M_g Molar mass of the gas
M_{hkl} Multiplicity factor
M_o Total mass of the particles
m_p^o Mass flow rate
n Total number of measurements
n_c Critical speed
n_e Number density of electrons
n_x Ranking of a sample failing at strength x
P Load
P Packing factor
P_a Atmospheric pressure
p_e Partial pressure of the plasma
Pe Exit pressure
Pi Inlet gas pressure, density of the ith phase
P_m Hardness of the softer counterpart
P^P Packing factor of the pure phase
P_t Throat pressure
$P(x)$ Probability of the element under test to support a load x
ϕ_c Work function
Q Heat energy, heat flux
Q_0 Specific energy of ignition
q_l Feed rate
ρ Density
ρ_g Gas density
ρ_m Fluid density
ρ_p Particle density
R Gas constant, radius of the ball mill container, radius of the goniometer
R_a Roughness
RA Relative accuracy

R_{et} Particle Reynolds number
R_{th} Thermal contact resistance
r/r_m Radius of the particle, radius of the ball, roughness, base radius
σ Electron conductivity in plasma
σ_d Standard deviation
σ_f Fracture stress
S,e Spalt thickness
s Solid layer thickness, separation distance between the slits
t Thickness of the coating
T_c Cathode temperature
T_s Substrate temperature
T_t Melting point of the splat
ΔT Temperature change
T_{gi} Initial gas temperature
T_p Particle temperature
θ Water contact angle
Θ Solidification parameter
u Fluid viscosity, coefficient of friction
u_g Gas velocity
u_{gi} Initial gas velocity
u_p Velocity of particle
V Volume of the particle
V_a Unit cell volume
V_f^t Volume fraction of tetragonal ZrO_2
V_i Effective diffraction volume
v Relative velocity of the torch (w.r.t. substrate)
v Sonic velocity, fluid viscosity, frequency, Poisson's ratio
v_I Injection velocity of the slurry
v_i Specific volume of gas
v_t Terminal velocity
W Work of adhesion
w Angular velocity
W_e Weber number
W_i Weight fraction
X_a Amorphous fraction
$\overline{x}$ Mean
X_i Weight fraction of ith component
X_{ic} Refined weight fraction
X_m Mass absorption coefficient
x_o Characteristic stress
X_{sc} Refined weight fraction of the internal standard
X_s Weight fraction of the original internal standard
x_u Minimum stress required for failure
ξ Degree of flattening



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Introduction

Fundamentals of Thermal Spraying discusses the thermal spraying concept, and its uses are explained elaborately. Starting from the historical development of thermal spraying, the book is very comprehensive and is pitched more at the informed reader. Herein, self-explaining schematics highlight the conceptual notes and depict the concepts deeply for better understanding for graduates of programs including Materials Science and Engineering, Metallurgical Engineering, Mechanical Engineering, Production and Manufacturing Engineering, and Design. It also aims at the staff of companies that are specifically working on surface engineering with thermal spraying. The chapters include schematics, keeping undergraduate students in mind for its adoption as a textbook. Each aspect, from starting powder, spraying parameters, diagnostics and coating deposition, is provided for in-depth understanding. The major parts of the instrumentation, the spraying gun, which is the fundamental aspect of different thermal spraying conditions, are discussed as well. Solved examples, numerical problems and descriptive questions are included for self-assessment for the purpose of self-learning. Important case studies from domains including aerospace, biomedical, manufacturing, wettability and so on are highlighted with practical application of thermally sprayed coatings. Thus, the book can inspire and motivate readers to become involved in the research and development of thermal spray coatings.



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1 Development of Thermal Spray Techniques and Applications

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Surface engineering, a broad sub-discipline of Materials Science, encompasses several methods and techniques to modify the properties of a solid surface. The motivation to alter surface properties is to enhance their interaction with the environment, be it via force, heat, electricity, magnetic fields, biological interaction and so forth. Among others, thermal spraying is an important surface engineering technique with widespread industrial applications. This chapter covers the origins of thermal spraying, its evolution, the emergence of new spraying techniques and some of its leading applications across industries.

1.1 SCHOOP'S PATENT AND GUN DESIGN

The idea of spraying metallic particles to obtain homogeneous and continuous deposits on a substrate is accredited to the Swiss inventor Max Ulrich Schoop. In 1909, he filed two patents, one in Switzerland and another in Germany, explaining the design for spraying process (metal), which delivers metallic coating with highly dense structure [1]. Chronologically, flame spraying is the *first* spraying technique developed by Schoop. The patents were described in a process with an oxyacetylene welding torch. He claimed that the invention was based on an observation made while seeing his children using Flobert guns for sport shooting. The lead bullets shot on their garden wall had formed, more or less, a connected coating. This prospect of being able to alter the properties of a surface excited Schoop to conduct experiments and verify its viability. Particularly, the modified process was described with a thin wire of lead and tin as the feed. Later, the powdered materials were utilized in the advanced torches of hot jet flow, where it heated while being accelerated towards the substrate. In 1908, Schoop also patented an *electric arc–spraying* process to allow most of the metals and electrically conductive materials to be sprayed. The proper control on the electric arc–spraying process could be able to coat zinc on steel or stainless steel and lead to successful development of the metallizing industry for the prevention of the corrosion of structural components. After extensive research, Schoop explained the underlying mechanism as follows:

> "The fundamental principle of the present invention consists in imparting a high velocity to solid metal or metal oxide particles projected towards a non-porous surface not coated with adhesive, and not heated to the melting point of the particles, an intimate connection between the particles and the receptive surface being obtained by means of the violent impact."

Further, Schoop suggested that the action could be governed via accumulation of the external heat [2]. Some of the ways of achieving this included heating of:

- An agent with pressure carrying particles (vapor, compressed air or gas);
- The surface of the substrate (to be coated);
- Powder particles (before being discharged into the gun or during their flight).

For example, the powder particles added in stream of gases, which are ignited just as they exit the discharge nozzle. In this manner, the enthalpy content of the gases

would be transferred to the particles. As a result, these particles become more ductile and hence susceptible to deformation upon impact. Along similar lines, Schoop argued that the mixture containing air and metal could be heated with the help of a tube (generally electrically heated) or a flame that can be arranged at the exit from the delivery nozzle. For a flame, however, the difficulty would arise in ensuring homogeneous heating of the particles. Thus, Schoop's vision is commended for acknowledging that to deposit, it is not necessary for all particles to be in an entirely liquid state before impinging the surface. If subjected to adequate pressure, the particles (except those electrically non-conductive) are rendered a plasticity which is quite sufficient to form a soldering or fusion of particles among each other, which results in the formation of a uniform and continuous metallic layer. To execute the process described, he devised the apparatus illustrated in Figure 1.1. For inspiration, in those times it was natural for him to turn to appliances, such as the sand blasting apparatus used for surface treatment. The only resemblance Schoop's design had, however, was regarding the method of working and not in regard to the action. The effects produced by the two were completely different.

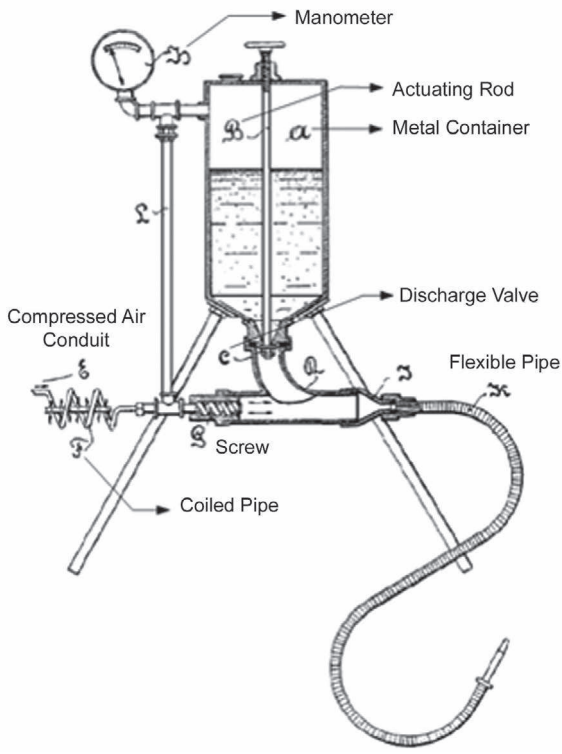


FIGURE 1.1 Schoop's apparatus for projecting powdered solid particles at very high pressures.

Source: Courtesy of JTST Historical Patent #22 United Kingdom patent office [3].

In engineering parts and components, the surface bears the brunt of all major interactions during use. It is the surface that first negotiates with the external stimuli; the bulk's role comes subsequently. This makes it highly vulnerable to a list of surface phenomena which could cause potential damage or degradation of the component. Functionalized coatings may be deposited in order to prolong the life of components and augment desired properties. Some of the essential motivations for coating structural parts include:

1. Improved functionality, for example, biocompatibility in titanium-based hip implants;
2. Improved component life by increasing wear, erosion and corrosion resistance;
3. The solution to previously insurmountable engineering problems;
4. Enhanced part life by salvaging worn-out parts;
5. Conservation of scarce material resources and reduction of component costs;
6. Reduction of power consumption and effluent output.

1.2 EVOLUTION OF THERMAL SPRAY TECHNIQUES

Thermal spray processes are explained as heating the particles to a fully molten or partially molten state followed by accelerating them toward a prepared surface with the help of pressurized gases or liquid atomization jets [3]. The high pressure from gases provides momentum to the particles, causing them to distort, flatten and subsequently fragment into smaller drops and ligaments. Upon impact on the substrate, these drops form splats which cool down to form lamellar structures. Successive impact of particles results in layers of many such lamellae which form the coating. The rate of cooling is in the order of 10^6 Ks^{-1} for metallic particles, though they generally exceed this magnitude. The nature of the bond could be either mechanical (topographical interlocking) or metallurgical (atomic bonding/diffusion).

1.3 DEVELOPMENT OF NEW PROCESSES

Today there exist several variants of thermal spray techniques which utilize either a high degree of superheating or very high particle velocities to deposit lamellar coatings. Densities as high as 99% can be achieved through these processes. The significant expansion of the thermal spray technology did not occur after the first development of the technique until 1945, more than three decades later. However, powder, electric arc and plasma spraying were developed and subsequently introduced in that development [4]. Improvements in thermal spray processes have been made with the basic operating principles developed by Schoop and other scientists. After World War II, powders are fed directly into the combustion flames of the system to generate high-velocity jets. The high-velocity jets will alter the characteristics of the coated materials. Other than the development in the thermal spray processing, additionally, tailoring of starting feedstock materials have improved the process. Figure 1.2 summarizes the development history

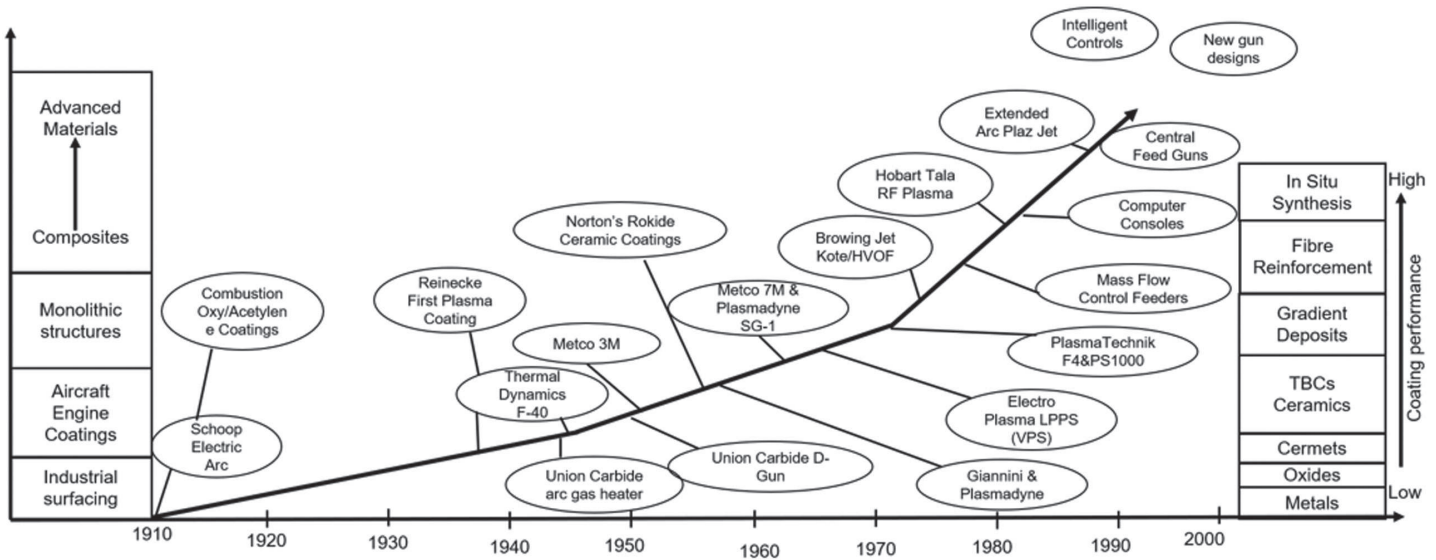


FIGURE 1.2 Timeline thermal spray developments, equipment and processes.

Source: Adapted and redrawn from [5].

of the thermal spray process, applications and materials, highlighting significant milestones in the area.

The selection and process parameters can be tweaked to realize porous coatings as well, which can be classified based on their source of heating as follows:

1. Flame spray: conventional and powder
2. Electric arc wire spray
3. Plasma spray
4. High-velocity oxy-fuel spray
5. Detonation gun spray.

1.3.1 Flame Spray

The evolution of combustion processes was driven by development in the scientific and technical innovations and the needs of the market. Historically three types were used: (1) flame spraying, (2) high-velocity oxy-fuel flame and (3) detonation spray. Flame spraying predominantly uses oxyacetylene torches that can achieve a premixed maximum combustion temperature of about 3,000 °C with flame velocities below 100 m/s. Spray gases common in use include acetylene, propane or hydrogen gas, along with oxygen. Generally, the sprays are fed into the spraying gun in the axial direction. The combustion spray guns are designed to perform feeding, acceleration, heating and providing direction to the flow of the material. In the powder flame spray, the spraying materials in powder form will be fed into the vicinity of flame. The powder particles are injected radially in the spray torch. Since most of the materials are available in powder form, the powder flame spray offers versatility in the aspect of utilization.

In the wire flame spray, the wire is axially fed into the spray torch so that it melts in the gaseous oxy-fuel flame. The only difference between the powder and wire flame–spray processes are the feeding materials. The feeding materials should be in the form of wire in wire flame spray. The flame temperatures and characteristics are determined by the ratio of oxygen to fuel gas and their pressures. The ratio determines whether the flame is oxidizing, neutral or carburizing. The molten droplets atomize upon interaction with the compressed air that also directs them towards the substrate. The shortcoming of the conventional combustion spraying process is that the maximum gas temperature is provided by the adiabatic flame temperature of the combustion gas mixture. So, it is limited for spraying materials with high melting temperatures, such as ceramics. Further, the environment of the combustion process can lead to chemical reactions between the spraying materials and the combustion gases. Still, flame spraying is a commonly used coating technique because it is economical.

1.3.2 Electric Arc Wire Spray

The electric arc (wire-arc) spray process uses wire as a feeder material. Heating is obtained by creating an arc between the wire and the electrode. In this process,

an arc is generated when two oppositely charged metallic wires are brought into contact. The resultant heat is sufficient to melt the feed, which is subsequently atomized and projected by compressed air onto a substrate ready to be coated. Exposure of metals in the harsh environment during the electric arc spraying was better controlled compared to that of flame spraying.

The coating composition can be tailored by the use of dissimilar metals or cored wires. In general, electric arc wire spraying exhibits higher bond strength than flame spraying. Electric arc wire spraying is advantageous over flame spraying in terms of providing a higher bond strength, deposition rate and deposition efficiency.

1.3.3 Plasma Spray

Interest in thermal spraying applications grew with the plasma spraying process introduced for the first time in 1939 by Reinecke. Prior to the development of plasma spraying, a confined arc gas heater was established. Primarily, it was developed to assist in cutting and joining as similar to the welding technology. An earlier plasma spray coating process was first demonstrated with the powders injected as the feed into a high-temperature plasma arc. The plasma arc could melt powder particles and accelerate the molten particles toward a substrate simultaneously. One of the advantages of plasma spraying was significantly higher process temperatures than that of the combustion spray. Also, there is no dependence of the feed material on the heat source, whereas feed material is completely dependent in the wire arc spray process. A high-frequency electric arc initiated between cathode (made of tungsten) and anode (water-cooled copper) ionizes the gas flowing in between, creating a high-pressure plasma. It is sustained using DC power. The gases considered for plasma generation include Ar, He, H_2 and N_2. At temperatures as high as 15,000 °C, the particles melt and are directed onto the workpiece.

Plasma processes have high heating potential and particle speed, which improve the coating quality. In the early 1980s, subsequent growth occurred in the applications of high-technology thermal spray. In the late 1950s, much of the thermal spray equipment technology saw its parallel and separate advancement in flame/combustion, electric arc and plasma spray. Successively, the detonation gun (D-Gun) process was introduced from the advancement in the arc gas heater technology for powder-spray applications. In the early 1970s, the plasma spray emerged as one of the most extensively used advanced technologies among thermal spray coatings. Thus, the developments in the plasma spray equipment as well as materials were aimed at for further advancement. Initially, the plasma spraying guns were designed with the maximum power of 40 kW, but the advancement in the equipment design improved the maximum to 250 kW. Also, continuous utilization of the system was enabled with effective water-cooling design and electrodes along with the use of high arc voltage. Simultaneously, plasma gas flow rates in the plasma guns have increased, and the speed of gas exit has promptly improved from subsonic to supersonic values. Successive increases in the particle

speeds due to high gas exit from the plasma gun increased the density and bond strength of the deposited coating. Moreover, the development rate of plasma spraying device is not so much. So, the research and development in thermal spray now focus on the process control, computer-controlled supports, real-time sensors for the process control, and automated or robot handling systems.

1.3.4 High-Velocity Oxy-Fuel Spray

Combustion spraying, with the exception of D-Gun, has caused an improvement with the development of high-velocity oxy fuel (HVOF) spraying system. The HVOF spray has enhanced the combustion spray jet by improving the particle temperatures. Also, the high speeds of molten particles are achieved through confinement of combusting gases and particles. The resulting high particle velocity and temperatures enhance the coating density and bond strengths. HVOF spraying is one of the coating processes that challenge the D-Gun and plasma spray coating processes in the coating technology. It is also reported that high particle speeds reduce the overheating of the particles. Ultimately, it leads to prevention of the oxidation and decarburization (in the case of carbides) which are mostly seen in the plasma-sprayed coatings.

Fuel gas, including propane, propylene, methyl-acetylene propadiene propane (MAPP), hydrogen or liquid kerosene, is burned in a chamber with the help of oxygen. Powder particles are introduced in the products of this combustion and projected towards the substrate with high-velocity compressed air. As the gas expands through a nozzle, it attains supersonic velocity which helps ensure dense coatings. The deposition mechanism is more dependent on plastic deformation of the particle rather than complete melting.

1.3.5 Detonation Gun Spray

Initially design of the D-Gun proved that it is capable of producing dense, reliable and adherent coatings with high bond strength among the thermal spray technologies. Till date, no process has emerged over the D-Gun process to produce efficient coatings. However, the recently developed HVOF coatings are challenging at this juncture. Before the beginning of the D-Gun process, aero-engine did not mention the type of thermal spray technique involved for the coating. It is just because of relatively high porosity and poor adherence of the coatings with the aero-engine components. But the plasma spray had experienced a similar application in many high-temperature materials with its high materials flexibility to process.

A mixture of oxygen and fuel gas (generally acetylene) is ignited through high-frequency cyclic (~10 times per second) sparks to cause detonations. The detonation waves so produced heat the particles and accelerate the powders to supersonic velocities as a result of their high temperature and high pressure. As the shock wave expands in all directions, the barrel is purged with nitrogen gas to avoid choking of the powder feed from the back end. Based on the application