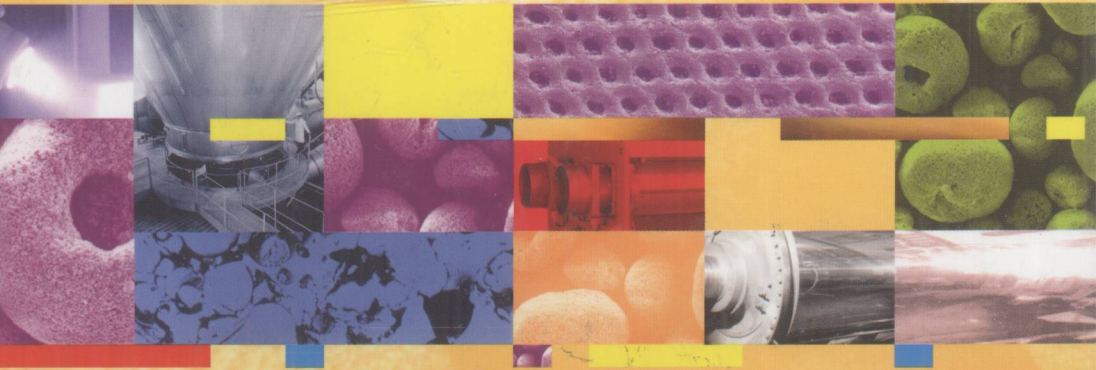


LECH PAWLOWSKI

THE SCIENCE AND ENGINEERING OF THERMAL SPRAY COATINGS



SECOND EDITION

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The Science and Engineering of Thermal Spray Coatings

Second Edition

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The Science and Engineering of Thermal Spray Coatings

Second Edition

To my wife Muryel and to my children Irene and David

Preface to the Second Edition

Since the first edition of *The Science and Engineering of Thermal Spray Coatings* was published in 1995, thermal spray technology has continued its scientific, technical and economic growth. The major laboratories have been equipped with diagnostic tools, enabling observation of individual particles and an intelligent optimization of spray processes. The modelling of the processes has progressed with the dissemination of sophisticated software and rapid computers. Nanotechnologies were introduced by an appropriate manufacturing of spray powders or by using powder suspensions. Finally, an understanding of the environmental impact of the technology has progressed considerably.

Technical progress is related mainly to the development of new spray techniques, such as, among others, the cold gas spray method, which enables obtaining many metal and alloy coatings with reduced oxidation and plasma spraying with axial injection of powders, which increases considerably the productivity of deposition. Many sophisticated methods of pre- and post-spray treatments and the coatings' characterization were introduced into industry in a routine way.

Economic progress is related to the new areas of coatings' applications. The sprayed coatings have gained a recognized place in the biomedical, chemical, printing and automobile industries. New applications will hopefully introduce the deposits into the electronics industry.

The first edition of the book was very well received and many people involved in the technology have used the book. More than 400 citations of this book in bibliographies are witness to its popularity and usefulness. The second edition is entirely rewritten by taking into account new developments, maturing of the technology and the author's views. Discussions with many colleagues have enabled me to refine the book's

content. Consequently, the chapter about the ‘organization of a spray workshop’ has been removed from this present edition.

I wish to thank the many students who have encouraged me to finish this second edition. My gratitude also goes to my Ph.D., graduate and undergraduate students, who have helped me in the realization of my scientific ideas; many of them being considered in the present book. In addition, many thanks also go to the copyright holders for their permission to re-use a number of figures. Last but not least, let me thank my family for supporting me during the writing of this book.

Lech Pawlowski
Lille, France
December, 2007

Preface to the First Edition

My contact with thermal spraying started in the autumn of 1973 when I was asked to choose the subject for an M.Sc. thesis. As were most of my fellow students at the Electronic Technology Institute of the Technical University of Wroclaw (Poland), I was attracted more by the technology of semiconductors. My tutor, Professor Licznarski, then changed my mind, by showing me very thick coatings and explaining the deposition technique of plasma spraying.

This deposition method is just one from the 'family' of thermal spraying techniques. Thermal spraying is now used in the research laboratories of many universities and also in industry. The laboratories will soon complete an understanding of the physical and chemical phenomena of spraying. Industry is exploring new applications of these coatings. The expansion of thermal spraying in the laboratories and in industry has created the need for this volume.

This book is therefore addressed to professionals at different educational levels. Highly trained researchers and engineers can find a physical background of thermal spraying processes, a description of coatings characterization techniques and an up-to-date review of the coatings properties.

The sales officers and technicians will hopefully appreciate the basic information concerning the consumables used in thermal spraying and the methods of pre- and post-spraying techniques.

Finally, the entrepreneur, who wishes to invest in thermal spray techniques will find a description of thermal spraying technology and remarks concerning the organization of a thermal spray workshop.

This book gives a complete description of the technology of thermal spraying, starting with a discussion of powder manufacturing and testing

techniques and the methods of pre-spray treatment. The most important techniques of thermal spraying in present use, as well as those in the research and development stage, are discussed. Finally, the techniques of post-spraying treatment, such as mechanical finishing, high-pressure and high-temperature treatments and laser treatment are outlined.

The book also explains the physics of thermal spraying and the phenomenon of acceleration of heating the solid particles in the flames. The problems related to the coatings build-up, which starts with the 'splash' of an individual particle through to the generation of thermal stresses in the coating, are also discussed. Special attention is given to the methods of coating characterization, including microstructure investigation, as well as the testing of mechanical and physical properties and non-destructive methods enabling control of their quality. The coatings' properties, determined by the methods discussed, their relation to the coatings' microstructure and processing parameters are systematically reviewed. Similarly, coating applications in such important branches of modern industry as aeronautics, printing, electronics and others are presented.

A chapter related to the creation and organization of a modern thermal spray workshop concludes the text.

Many people have contributed in a more or less direct way to the book's creation.

I wish to acknowledge the friendly support of Professor P. Fauchais, of the University of Limoges (France). I am equally grateful to Professor S. Sturlese who, together with other scientists of Centro Sviluppo Materiali in Rome (Italy), revised the reviews of thermal and electrical properties of the coatings, which are incorporated in this book.

Dr R.C. Tucker, Jr of Praxair ST in Indianapolis (IN, USA) kindly revised the chapter concerning the D-gunTM technique, while Dr K. Kirner from Gerlingen (Germany) contributed to the corrections of the proof-pages.

Ing. F. Kilp of Cermet Vertrieb OHG. in Düsseldorf (Germany) and Dr D. Lombard of Pechiney in Voreppe (France) made available their papers about the powder production methods. Professor A. Vardelle of the University of Limoges (France) provided the papers about the impact of sprayed particles, while Dr J. Tekeuchi of Tocalo in Kobe (Japan) made available the photographs of the coated rollers applied in the paper and steel industries.

I want to express my gratitude to the following colleagues and organizations who sent me the requested photographs and permitted me to use them as the figures in the book: Mr J. Andresen, Dr Ing.

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Many thanks to my wife Muryel for drawing many of the figures and her support and patience during the last months of the book's writing.

Lech Pawlowski
Nozay, France
August 1994

Acronyms, Abbreviations and Symbols

ACRONYMS/ABBREVIATIONS

1SLD	One-step laser deposition
2SLD	Two-step laser deposition
2-D	Two dimensional
3-D	Three dimensional
AA	Average roughness (see R_a)
AC	Alternating current
AEA	Acoustic emission analysis
AFM	Atomic force microscopy
AHF	Ability-of-heating factor (defined in Equation (5.32))
APS	Atmospheric plasma spraying
ARCI	Advanced Research Centre for Powder Metallurgy and New Materials, International (Hyderabad, India)
AS	Arc spraying
AZO	Aluminium zinc oxide
b.c.c.	Body-centred cubic
BET	Brunauer–Emmett–Teller (technique of porosity evaluation (see Table 7.7))
BIC	Bunsen ice calorimeter
BSE	Backscattered electron
c	Cubic
CAPS	Controlled-atmosphere plasma spraying
CaSZ	Calcium-stabilized zirconia
CBN	Cubic boron nitride

CCD	Charge-coupled device
CeSZ	Ceria-stabilized zirconia
CFD	Computational fluid dynamics
CGSM	Cold-gas spraying method
CLA	Central-line average (see R_a)
CP	Continuous pulse
CVD	Chemical vapour deposition
CW	Continuous wave
DC	Direct current
DCB	Double-cantilever beam
D-GUN	Detonation-gun spraying
DIC	Differential interference contrast
DMF	Difficulty-of-melting factor (defined in Equation (5.32))
DOE	Design of experiment
DSC	Differential scanning calorimetry
DT	Double torsion
DTA	Differential thermal analysis
e	Base of normal logarithm (≈ 2.718)
e-beam	Electron beam
EBPVD	Electron-beam physical vapour deposition
EDS	Energy-dispersive spectroscopy
EELS	Electron energy-loss spectroscopy
EMPA	Electron microprobe analysis
EXAFS	Extended X-ray absorption fine structure
f	Focus
F	Fuel
f.c.c.	Face-centred cubic
FS	Flame spraying
FS-powder	Flame spraying using a powder
FS-wire	Flame spraying using a wire
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
HA	Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$)
HAZ	Heat-affected zone
HBSS	Hank's balanced salt solution
h.c.p.	Hexagonal close-packed
HF	High frequency
HIP	Hot isostatic pressing
HOSP	Homogenous oven spherical powder
HPPS	High-power plasma spraying

HVAF	high-velocity air-fuel
HVOF	High-velocity oxy-fuel
HYPREPOC	Hydrogen-pressure-reducing powder coating
ICP	Inductively coupled plasma
ICPES	Inductively coupled plasma–emission spectroscopy
ID	Internal diameter
IPS	Inert plasma spraying
ir	Infrared
IRS	Infrared absorption spectroscopy
ITO	Indium tin oxide
L	Liquid
L2F	Laser Two Focus
LCVD	Laser-assisted chemical vapour deposition
LD	Line density
LDV	Laser Doppler velocimetry
LF	Laser-flash method of thermal diffusivity determination
LPPS	Low-pressure plasma spraying (see VPS)
LSP	Laser-shock processing
LTE	Local thermodynamic equilibrium
LV	Laser velocimetry
Mag	Magnification
MB	Modulated-beam method of thermal diffusivity determination
MF	Mechanofusion
MgSZ	Magnesia-stabilized zirconia
MIP	Mercury-intrusion porosimetry
MMC	Metal–matrix composite
MOCVD	Metal–organic chemical vapour deposition
NDT	Non-destructive testing
NIC	Nomarski interference contrast
OM	Optical microscopy
PECVD	Plasma-enhanced chemical vapour deposition
PLD	Pulsed-laser deposition
PVD	Physical vapour deposition
PTA	Plasma-transferred arc
PZT	Lead–zirconate–titanate
R	Alkyl group, C_nH_{2n+1} , e.g. CH_3 or C_2H_5
RF	Radiofrequency
rpm	Rotations per minute

RS	Raman spectroscopy
RT	Room temperature
SAD	Selected area diffraction
SAW	Surface acoustic wave
SBF	Simulated body fluid
SCE	Standard calomel electrode
ScSZ	Scandia-stabilized zirconia
SE	Secondary electron
SEM	Scanning electron microscopy
SHS	Self-propagating high-temperature synthesis
SIMS	Secondary-ion mass spectrometry
slpm	Standard litre per minute
SOFC	Solid-oxide fuel cell
SPS	Shrouded plasma spraying
STM	Scanning tunnelling microscopy
t	Tetragonal
t'	Tetragonal non-transferable phase of sprayed stabilized ZrO_2
TAT	Tensile adhesion test
TBC	Thermal-barrier coating
TCP	Tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$)
TEM	Transverse electromagnetic (wave); transmission electron microscopy
TGA	Thermogravimetric analysis
TGO	Thermally grown oxide
TSC	Thermally sprayed composite
TSR	Thermal shock resistance
TTBC	Thick thermal-barrier coating
TTCP	Tetracalcium phosphate ($\text{Ca}_4\text{P}_2\text{O}_9$)
UPS	Underwater plasma spraying
uv	Ultraviolet
VPS	Vacuum plasma spraying (see LPPS)
WDS	Wavelength-dispersive spectroscopy
WSP	Water-stabilized plasma
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
YAG	Yttrium aluminum garnet
YBCO	$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$
YSZ	Yttria-stabilized zirconia

TRADE NAMES

Amdry TM	Powder(s), manufactured by Sulzer Metco, Wohlen, Switzerland
Amperit TM	Powder(s), manufactured by HC Starck, Goslar, Germany
Axial III TM	Plasma torch, commercialized by Northwestern Mettech, Richmond, BC, Canada
D-gun TM	Detonation spray technique, used by Praxair ST, Appleton, WI, USA
DPV-2000 TM	Diagnostic tool enabling temperature and velocity to be determined, commercialized by Tecnar, St-Bruno, QU, Canada
JetStar TM	HVAF spray technique, used and commercialized by Praxair ST, Appleton, WI, USA
Laserblast TM	Laser installation, for cleaning and activation of surfaces, Quantel, Les Ulis, France
Plazjet TM	High-enthalpy spray torch, commercialized by TAFA, Concord, NH, USA
PROTAL TM	Surface activation by laser ablation, Sulzer Metco, Wohlen, Switzerland and the University of Belfort-Montbéliard, France
Rokide TM	Flame spraying of ceramic rods, Saint Gobain, La Défense, France
RotaPlasma TM	Plasma spraying of the internal parts of cylinder bores with a jet rotating around the cylinder axis, developed and commercialized by Sulzer Metco, Wohlen, Switzerland
Sonarc TM	Spray technique (a combination of AS and HVOF), developed at the University of Dortmund, Germany
SprayWatch TM	Diagnostic tool enabling temperature and velocity to be determined, commercialized by Oseir, Tampere, Finland
Super D-gun TM	Spray technique (a further development of D-gun TM), used by Praxair ST, Appleton, WI, USA
Triplex TM	Plasma spray torch, developed by Professor K Landes, Munich, Germany and used by Sulzer Metco, Wohlen, Switzerland

SYMBOLS^{1,2}

$\Delta_f H^O$	Standard enthalpy of formation
Δx	Variation of variable x
a	Fraction of absorbed energy (see Equation (4.4)) or diffusivity (see Equation (4.5))
A	Constant
B	Magnetic induction
Bi	Biot number (defined in Equation (5.30))
c	Velocity of sound or velocity of light (see Equation (5.46))
c_p	Specific heat under constant pressure (defined in Equation (7.21))
c_v	Specific heat at constant volume
C	Capacity
C_D	Drag coefficient (see Equation (5.13))
d	Diameter or thickness (see Equation (7.29))
$div(\vec{v})$	$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$
e	Charge on an electron (1.602×10^{-19} C)
$\vec{e}_x, \vec{e}_y, \vec{e}_z$	Unitary vectors in x -, y -, z -directions
E	Energy; elastic modulus (see Equation (6.18)); electric field
f	Frequency
F	Force
Fro	Froude number (defined in Equation (1.9))
g	Gravitation constant (9.81 m/s^2)
$\overrightarrow{grad}(v)$	$\frac{\partial v \vec{e}_x}{\partial x} + \frac{\partial v \vec{e}_y}{\partial y} + \frac{\partial v \vec{e}_z}{\partial z}$
G_i	Interfacial fracture energy
G_{1c}	Critical energy per unit area at crack propagation for mode-1 fracture
h	Static enthalpy; heat transfer coefficient (see Equation (5.28)); Planck constant ($6.6262 \times 10^{-34} \text{ J s}$); thickness of lamella
H	Total enthalpy; hardness (see Equations (7.11) and (7.12)); magnetic field intensity

¹ Symbols with arrows above – vectors; symbols without arrows above – scalar quantities.

² In some cases, symbols are also explained in the text and/or figures.

H_{ev}	Enthalpy of evaporation
H_{m}	Enthalpy of melting
HK	Knoop hardness
HRC	Rockwell hardness
HV_c	Vickers microhardness, under a load of c Newtons
i	Integer number
I	Electric current; intensity of radiation
j	Current density
k	Kinetic energy of turbulent flow; reaction constant (see Equation (5.8)); Boltzmann constant (1.38×10^{-23} J/K)
K	Quality of laser beam (see Equation (4.3)); toughness
K_{1c}	Critical stress intensity factor (fracture toughness) at mode 1 of fracture
Kn	Knudsen number (defined in Equation (5.20))
l	Length; distance; path
L	Optical absorption depth at which the power density decreases by a factor of $1/e$ (see Equation (4.4))
m	Mass
M	Mach number (v/c)
n	Integer number
N	Integer number; concentration
Nu	Nusselt number (defined in Equation (5.28))
p	Pressure
p^*	Vapour pressure
P	Porosity; power
Pr	Prandtl number (defined in Equation (5.29))
q	Feed rate; flow rate; power density (see Equation 4.5)); heat flux (see Equations (5.12) and (7.24))
r	Radius; variable in cylindrical and spherical systems of coordinates
R	Reflectivity; radius; universal gas constant (≈ 8.314 J/(mol K)); resistance
R_a	Average roughness, defined as the arithmetical average of the absolute values of the amplitudes of the surface with regard to a mean line along the measured distance
R_i	Rate of generation of the chemical species per unit volume (see Equation (5.1))
R_{max}	Maximum roughness, defined as the 'deepest valley' in the surface inside the measured distance
R_s	Sheet resistance