

Robert B. Heimann

 WILEY-VCH

# Plasma Spray Coating

Principles and Applications

Second, Completely Revised and Enlarged Edition



# Plasma- Spray Coating

by. Robert B. Heimann

Copyright© VCH Verlagsgesellschaft mbH. 1996

Robert B. Heimann

Plasma-Spray Coating



# Related Reading

Brook, R. J.

## **Processing of Ceramics**

Volumes 17 A and B from the series *Materials Science and Technology*, R. W. Cahn, P. Haasen, E. J. Kramer (eds.), VCH, 1995, ISBN 3-527-26830-8 and 3-527-29356-6.

Cahn, R. W. (ed.)

## **Processing of Metals and Alloys**

Volumes 15 from the series *Materials Science and Technology*, R. W. Cahn, P. Haasen, E. J. Kramer (eds.), VCH, 1992, ISBN 3-527-26828-6.

A. C. Jones, P. O'Brian

## **CVD of Compound Semiconductors. Precursor Synthesis, Development and Applications.** VCH, 1996, ISBN 3-527-29294-2.

T. Kodas, M. Hampden-Smith

## **The Chemistry of Metal CVD.** VCH, 1994, ISBN 3-527-29071-0.

## **Materialwissenschaften und Werkstofftechnik. Entwicklung, Fertigung, Prüfung, Eigenschaften und Anwendungen technischer Werkstoffe.**

VCH, Volume 27, 1996, ISSN 0933-5137.

## **Materials and Corrosion.** VCH, Volume 47, 1996, ISSN 0043-2822.

## **Chemical Vapor Deposition.** Published bimonthly as part of **Advanced Materials.** VCH, Volume 2, 1996, ISSN 0948-1907

© VCH Verlagsgesellschaft mbH, D-69451 Weinheim (Federal Republic of Germany), 1996

### Distribution:

VCH, P.O. Box 10 11 61, D-69451 Weinheim (Federal Republic of Germany)

Switzerland: VCH, P.O. Box, CH-4020 Basel (Switzerland)

United Kingdom and Ireland: VCH (UK) Ltd., 8 Wellington Court, Cambridge CB1 1HZ (England)

USA and Canada: VCH, 220 East 23rd Street, New York, NY 10010-4606 (USA)

Japan: VCH, Eikow Building, 10-9 Hongo 1-chome, Bunkyo-ku, Tokyo 113 (Japan)

ISBN 3-527-29430-9

Robert B. Heimann

# Plasma-Spray Coating

Principles and Applications



Weinheim • New York • Basel • Cambridge • Tokyo

Prof. Dr. Robert B. Heimann  
Institut für Mineralogie  
TU Bergakademie Freiberg  
Brennhausgasse 14  
09596 Freiberg  
Germany

This book was carefully produced. Nevertheless, author and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Published jointly by  
VCH Verlagsgesellschaft mbH, Weinheim (Federal Republic of Germany)  
VCH Publishers, Inc., New York, NY (USA)

Editorial Directors: Dr. Peter Gregory, Dr. Ute Anton  
Production Manager: Dipl.-Ing. (FH) Hans Jörg Maier

Every effort has been made to trace the owners of copyrighted material; however, in some cases this has proved impossible. We take this opportunity to offer our apologies to any copyright holders whose rights we may have unwittingly infringed.

Library of Congress Card No. applied for.

A catalogue record for this book is available from the British Library.

Deutsche Bibliothek Cataloguing-in-Publication Data:

Heimann, Robert B.:

Plasma spray coating: principles and applications / Robert B. Heimann. – Weinheim; New York; Basel; Cambridge; Tokyo: VCH, 1996

ISBN 3-527-29430-9

© VCH Verlagsgesellschaft mbH. D-69451 Weinheim (Federal Republic of Germany), 1996

Printed on acid-free and chlorine-free paper.

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine-readable language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition: Asco Trade Typesetting Limited, Hong Kong. Printing: betz druck gmbh, D-64291 Darmstadt

Printed in the Federal Republic of Germany.

# Preface

Thermal spraying encompasses a variety of apparently simple surface engineering processes by which solid materials (wire, rods, particles) are rapidly heated by a plasma jet or a combustion flame, melted and propelled against the substrate to be coated. Rapid solidification of the molten particles at the substrate surface builds up, splat by splat, into a layer which may have various functions including protection against wear, erosion, corrosion and thermal or chemical degradation. The coating may also impart special electrical, magnetic or decorative properties to the substrate. Thick coatings are applied in many industrial areas to restore or attain desired workpiece dimensions and specifications.

The text has been written bearing in mind the theoretical and practical requirements of students of materials engineering and materials science. It has been developed from the topics presented to classes of Master students of the Materials Engineering Program at the School of Energy and Materials, King Mongkut's Institute of Technology Thonburi, Bangkok, Thailand between 1991 and 1995 as well as to students of Technical (Applied) Mineralogy at Freiberg University of Mining and Technology since 1993. The author has also gained experience in plasma spray technology during his work from 1987 to 1988 as the head of the Industrial Products and Materials Section of the Industrial Technologies Department of the Alberta Research Council, Edmonton, Alberta, Canada, and from 1988 to 1993 as the manager of the Institutional and International Programs Group of the Manufacturing Technologies Department of the same organization.

It is nearly impossible to consider the entire body of literature on the subject of thermal spraying. Therefore, instead of an exhaustive coverage of applications of plasma-sprayed coatings only typical examples and case studies will be given to illustrate the various physical processes and phenomena occurring within the realm of this technology.

Many colleagues and friends helped with the production of this text. I owe thanks to Professor Dr. Dr. h.c. Walter Heywang, formerly director of Corporate Research and Development of Siemens AG in Munich for suggesting the idea of this book. I am much indebted to Mr. Liang Huguong, Dr. Ulrich Kreher and Mr. Dirk Kurtenbach who prepared diligently the numerous diagrams and graphs. The critical comments of my graduate students and Professor Jürgen Niklas, Institute of Experimental Physics, Freiberg University of Mining and Technology were most

welcome. My wife Giesela patiently endured my idiosyncrasies and irritations during some phases of the preparation of this text, and suffered through many lonely weekends. Last but not least, VCH Weinheim, represented by Frau Dr. Ute Anton, supported and encouraged me in the endeavour to complete the manuscript. Special thanks are due to Tommaso Albinoni and Antonio Vivaldi.

Robert B. Heimann

Freiberg, March 1996

# Contents

<b>List of Symbols and Abbreviations</b> . . . . .	xiii
<b>1 Introduction</b> . . . . .	1
1.1 Coatings in the Industrial Environment . . . . .	2
1.2 Surface Coating Techniques . . . . .	3
1.3 Brief History of Thermal Spraying . . . . .	8
1.4 Synergistic Nature of Coatings. . . . .	13
1.5 Applications of Thermally Sprayed Coatings . . . . .	14
References . . . . .	15
<b>2 Principles of Thermal Spraying.</b> . . . . .	17
2.1 Characterization of Flame versus Plasma Spraying . . . . .	21
2.2 Concept of Energy Transfer Processes . . . . .	22
2.3 Unique Features of the Plasma Spray Process . . . . .	22
References . . . . .	25
<b>3 The First Energy Transfer Process: Electron–Gas Interactions</b> . . . . .	27
3.1 The Plasma State . . . . .	27
3.1.1 Characteristic Plasma Parameters . . . . .	28
3.1.1.1 Langmuir Plasma Frequency . . . . .	28
3.1.1.2 Debye Screening Length . . . . .	29
3.1.1.3 Landau Length . . . . .	29
3.1.1.4 Collision Path Length . . . . .	30
3.1.1.5 Collision Frequency . . . . .	31
3.1.2 Classification of Plasmas . . . . .	31
3.1.2.1 Low Density Plasmas. . . . .	32
3.1.2.2 Medium Density Plasmas . . . . .	32



3.1.2.3	High Density Plasmas . . . . .	35
3.1.3	Equilibrium and Nonequilibrium Plasmas. . . . .	35
3.1.4	Maxwellian Distribution of Plasma Energies . . . . .	37
3.1.5	Equilibrium Compositions of Plasma Gases (Phase Diagrams). . . . .	38
3.2	Plasma Generation. . . . .	38
3.2.1	Plasma Generation through Application of Heat. . . . .	40
3.2.2	Plasma Generation through Compression. . . . .	43
3.2.3	Plasma Generation by Radiation. . . . .	43
3.2.4	Plasma Generation by Electric Currents (Gas Discharges). . . . .	44
3.2.4.1	Glow Discharges. . . . .	45
3.2.4.2	Arc Discharges . . . . .	46
3.2.4.3	Modeling of the Arc Column . . . . .	48
3.2.4.4	Structure of the Arc Column . . . . .	50
3.3	Design of Plasmatrons . . . . .	55
3.3.1	Arc Discharge Generators and their Applications . . . . .	57
3.3.1.1	Electrode-supported Plasmas . . . . .	59
3.3.1.2	Electrodeless Plasmas. . . . .	63
3.3.1.3	Hybrid Devices . . . . .	66
3.3.2	Stabilization of Plasma Arcs. . . . .	68
3.3.2.1	Wall-stabilized Arcs . . . . .	68
3.3.2.2	Convection-stabilized Arcs . . . . .	68
3.3.2.3	Electrode-stabilized Arcs . . . . .	69
3.3.2.4	Other Stabilization Methods . . . . .	69
3.3.3	Temperature and Velocity Distribution in a Plasma Jet . . . . .	70
3.3.3.1	Turbulent Jets . . . . .	70
3.3.3.2	Quasi-laminar Jets . . . . .	74
3.4	Plasma Diagnostics: Temperature, Enthalpy, and Velocity Measurements . . . . .	77
3.4.1	Temperature Measurements. . . . .	77
3.4.1.1	Spectroscopic Methods . . . . .	77
3.4.1.2	Two-wavelength Pyrometry . . . . .	80
3.4.2	Velocity Measurements . . . . .	81
3.4.2.1	Enthalpy Probe and Pitot Tube Techniques . . . . .	81
3.4.2.2	Laser Doppler Anemometry (LDA) . . . . .	83
3.4.2.3	Other Methods . . . . .	88
	References . . . . .	88
<b>4</b>	<b>The Second Energy Transfer Process: Plasma–Particle Interactions . . . . .</b>	<b>91</b>
4.1	Injection of Powders . . . . .	91
4.2	Feed Material Characteristics . . . . .	91

4.2.1	Solid Wires, Rods and Filled Wires. . . . .	94
4.2.2	Powders . . . . .	94
4.2.2.1	Atomization. . . . .	97
4.2.2.2	Fusion and Crushing . . . . .	97
4.2.2.3	Compositing . . . . .	100
4.2.2.4	Agglomeration . . . . .	100
4.3	Momentum Transfer . . . . .	100
4.3.1	Connected Energy Transmission . . . . .	100
4.3.2	Modeling of Momentum Transfer . . . . .	101
4.3.3	Estimation of the Drag Coefficient . . . . .	103
4.3.4	Surface Ablation of Particles . . . . .	104
4.4	Heat Transfer . . . . .	106
4.4.1	Heat Transfer under Low Loading Conditions. . . . .	106
4.4.2	Exact Solution of Heat Transfer Equations . . . . .	113
4.4.2.1	Particle Heating without Evaporation . . . . .	114
4.4.2.2	Particle Heating with Evaporation . . . . .	117
4.4.2.3	Evaporation Time of a Particle . . . . .	118
4.4.3	Heat Transfer under Dense Loading Conditions . . . . .	119
4.4.3.1	Conservation Equations . . . . .	121
4.4.3.2	Results of Modeling under Dense Loading Conditions . . . . .	122
4.4.4	Heat Transfer Catastrophy . . . . .	122
4.4.5	Energy Economy . . . . .	126
4.5	Particle Diagnostics: Velocity, Temperature, and Number Densities . . . . .	128
4.5.1	Particle Velocity Determination . . . . .	128
4.5.2	Particle Temperature Determination . . . . .	132
4.5.3	Particle Number Density Determination . . . . .	132
	References . . . . .	134
<b>5</b>	<b>The Third Energy Transfer Process: Particle–Substrate Interactions. . . . .</b>	<b>137</b>
5.1	Basic Considerations . . . . .	137
5.2	Estimation of Particle Number Density . . . . .	138
5.3	Momentum Transfer from Particles to Substrate . . . . .	141
5.4	Heat Transfer from Particles to Substrate . . . . .	149
5.4.1	Generalized Heat Transfer Equation . . . . .	150
5.4.2	Heat Transfer from Coating to Substrate . . . . .	151
5.5	Coating Diagnostics: Microstructure, Porosity, Adhesion, and Residual Stresses. . . . .	153

5.5.1	Microstructure of Coatings . . . . .	153
5.5.1.1	Splat Configuration . . . . .	154
5.5.1.2	Surface Roughness of Coatings . . . . .	155
5.5.1.3	Fractal Properties of Surfaces . . . . .	158
5.5.2	Porosity of Coatings . . . . .	164
5.5.2.1	Point Counting . . . . .	165
5.5.2.2	Mercury Pressure Porosimetry . . . . .	166
5.5.2.3	Archimedes' Method . . . . .	166
5.5.3	Adhesion of Coatings. . . . .	167
5.5.4	Chemical Changes . . . . .	168
5.5.5	Residual Stresses. . . . .	169
5.5.5.1	Blind Hole Test . . . . .	170
5.5.5.2	X-ray Diffraction Measurements ( $\sin^2 \psi$ -Technique) . . . . .	171
5.5.5.3	Almen-type Test . . . . .	174
5.5.5.4	Theoretical Analysis of Residual Stresses . . . . .	175
	References . . . . .	178
<b>6</b>	<b>The Technology Transfer Process: Solutions to Industrial Problems . .</b>	<b>181</b>
6.1	Wear- and Corrosion-Resistant Coatings . . . . .	181
6.1.1	Pure Carbides . . . . .	181
6.1.2	Cemented Carbides . . . . .	182
6.1.2.1	Tungsten Carbide/Cobalt Coatings. . . . .	183
6.1.2.2	Titanium Carbide-based Coatings . . . . .	191
6.1.2.3	Chromium Carbide-based Coatings . . . . .	196
6.1.2.4	Boride-based Coatings . . . . .	200
6.1.3	Oxide Coatings . . . . .	201
6.1.3.1	Alumina-based Coatings . . . . .	202
6.1.3.2	Chromia-based Coatings . . . . .	204
6.1.4	Metallic Coatings . . . . .	205
6.1.4.1	Refractory Metal Coatings . . . . .	205
6.1.4.2	Superalloy Coatings . . . . .	206
6.1.5	Diamond Coatings. . . . .	207
6.2	Thermal and Chemical Barrier Coatings . . . . .	209
6.2.1	Ytria-Partially Stabilized Zirconia Coatings (Y-PSZ) . . . . .	209
6.2.1.1	Stress Control and Modeling . . . . .	213
6.2.1.2	Sealing of As-sprayed Surfaces. . . . .	218
6.2.1.3	Laser Surface Remelting of Y-PSZ Coatings . . . . .	218
6.2.2	Other Thermal Barrier Coatings . . . . .	223
6.3	Bioceramic Coatings . . . . .	224
6.3.1	Thin Film Techniques for HAp Coatings . . . . .	225
6.3.1.1	Ion Beam Dynamic Mixing . . . . .	225

6.3.1.2	RF Sputtering . . . . .	225
6.3.1.3	Liquid Immersion Techniques . . . . .	225
6.3.1.4	Electrophoretic Deposition . . . . .	225
6.3.2	Thick HAp Coatings . . . . .	226
6.3.2.1	Plasma Sprayed HAp Coatings . . . . .	226
6.4	Functional Plasma-Sprayed Coatings. . . . .	232
6.4.1	HT-superconducting (HTSC) Coatings . . . . .	232
6.4.2	Coating for Solid Oxide Fuel Cells (SOFCs). . . . .	233
	References . . . . .	237
<b>7</b>	<b>Quality Control and Assurance Procedures.</b> . . . . .	<b>243</b>
7.1	Quality Implementation . . . . .	243
7.1.1	Total Quality Management . . . . .	243
7.1.1.1	Quality Tools . . . . .	243
7.1.1.2	Quality Philosophy. . . . .	244
7.1.1.3	Management Style . . . . .	245
7.1.2	Qualification Procedures . . . . .	245
7.1.3	Powder Characterization . . . . .	246
7.2	Characterization and Test Procedures . . . . .	247
7.2.1	Mechanical Properties . . . . .	248
7.2.1.1	Bond Strength . . . . .	248
7.2.1.2	Macro- and Microhardness Tests . . . . .	261
7.2.1.3	Fracture Toughness . . . . .	266
7.2.2	Tribological Properties . . . . .	268
7.2.2.1	Simulation of Basic Wear Mechanisms . . . . .	269
7.2.3	Chemical Properties . . . . .	275
7.2.3.1	Chemical Corrosion Evaluation Tests . . . . .	279
7.2.3.2	Burner Rig Test . . . . .	279
	References . . . . .	282
<b>8</b>	<b>Design of Novel Coatings</b> . . . . .	<b>285</b>
8.1	Coating Requirements . . . . .	285
8.2	Design of Novel Advanced Layered Coatings . . . . .	286
8.2.1	Gradient Layers . . . . .	287
8.2.2	Layered Materials in Thermodynamic Equilibrium. . . . .	288
8.2.3	Extended Solid Solution . . . . .	288
8.2.4	Multilayers . . . . .	288
8.3	Principles of Statistical Design of Experiments. . . . .	288

8.3.1	The Experimental Environment and its Evolution . . . . .	288
8.3.1.1	Screening Designs . . . . .	289
8.3.1.2	Response Surface Designs. . . . .	290
8.3.1.3	Theoretical Models. . . . .	290
8.3.2	Screening Designs . . . . .	291
8.3.3	Factorial Designs . . . . .	293
8.3.3.1	Full Factorial Designs . . . . .	293
8.3.3.2	Fractional Factorial Designs . . . . .	293
8.3.4	Box–Behnken Designs . . . . .	294
8.3.5	Designs of Higher Dimensionality . . . . .	295
8.4	Optimization of Coating Properties: Case Studies . . . . .	296
8.4.1	Plackett–Burman (Taguchi) Screening Designs . . . . .	296
8.4.2	Full Factorial Designs . . . . .	297
8.4.3	Fractional Factorial Designs . . . . .	299
8.4.3.1	Tungsten Carbide/Cobalt Coatings. . . . .	299
8.4.3.2	Ferrosilicon Coatings. . . . .	303
8.4.3.3	Alumina/titania Coatings . . . . .	305
8.4.3.4	Stellite Coatings . . . . .	308
8.4.3.5	Titanium Coatings . . . . .	309
8.5	Future Developments. . . . .	310
	References . . . . .	314
<b>A</b>	<b>Appendix A: Dimensionless Groups . . . . .</b>	<b>317</b>
	References . . . . .	318
<b>B</b>	<b>Appendix B: Calculation of Temperature Profiles of Coatings . . . . .</b>	<b>319</b>
B.1	Heat Conduction Equations. . . . .	319
B.2	Solutions of the Equations . . . . .	320
B.2.1	Substrate Temperature Profile . . . . .	320
B.2.2	Deposit Temperature Profile . . . . .	320
B.3	Real Temperature Profiles. . . . .	322
	References . . . . .	322
<b>C</b>	<b>Appendix C: Calculation of Factor Effects for a Fractional Factorial Design <math>2^{8-4}</math> . . . . .</b>	<b>323</b>
<b>Index</b>	. . . . .	<b>327</b>

# List of Symbols and Abbreviations

a.c. = alternating current  
AE = acoustic emission  
AJD = anode jet dominated  
APS = air plasma spraying  
BE = back wall echo  
CAPS = controlled atmosphere plasma spraying  
CBC = chemical barrier coatings  
CCF = cross-correlation function  
CFC = carbon fiber composite  
CJD = cathode jet dominated  
CSZ = completely stabilized zirconia  
CTE = coefficient of thermal expansion  
CVD = chemical vapor deposition  
CW-PTR = continuous wave photothermal radiometry  
d.c. = direct current  
E, EM, M, T, and S = plasma types  
EB-PVD = electron beam PVD  
ECM = electrochemical machining  
EMI = electromagnetic interference  
EP = electrode plasma  
f.c.c. = face centered cubic  
FFT = fast Fourier transform  
FGM = functional gradient material  
FPA = fracture profile analysis  
FTIR = Fourier transformed infrared  
HAp = hydroxyapatite  
HOSP = hollow-spherical-powder  
HPPS = high power plasma spraying  
HRC = Rockwell hardness  
HTSC = high temperature superconducting coatings  
HV = Vickers' hardness  
HVOF = hypervelocity oxyfuel gun  
ICP = inductively coupled plasma

IE = interfacial echo  
IGPS = inert gas plasma spraying  
IPS = inductive plasma spraying  
JIT = just-in-time  
LCF = low cycle fatigue  
LDA = laser Doppler anemometry  
LPPS = low pressure plasma spraying  
LPS = laser plasma spraying  
LTE = local thermodynamic equilibrium  
MHD = magnetohydrodynamic  
MRP = main regime parameters  
OCTA = oxide-cobalt-titanium anodes  
ORTA = oxide-ruthenium-titanium anodes  
p.p.m. = parts per million  
PA-CVD = plasma assisted CVD  
PAVD = plasma assisted vapor deposition  
PEN = positive electrode-electrolyte-negative electrode  
PLZT = lead lanthanum zirconate titanate  
PMMA = polymethylmethacrylate  
PMRS = plasma melted rapidly solidified  
PSI = particle-source-in (model)  
PSZ = partially stabilized zirconia  
PTA = plasma transferred arc  
PVD = physical vapor deposition  
PZT = lead zirconate titanate  
QFD = quality function deployment  
RFS = radio frequency spraying  
RT = room temperature  
SCFH = standard cubic feet per hour  
SDE = statistical design of experiments  
SEM = scanning electron microscopy  
SES = statistical experimental strategy  
SIA = slit island analysis  
SLPM = standard litres per minute  
SME = small and medium sized enterprises  
SOFC = solid oxide fuel cell  
SPC = statistical process control  
SPE = solid particle erosion  
SPS = shrouded plasma spraying  
SQA = statistical quality assurance  
SQC = statistical quality control  
STF = strain to fracture  
TBC = thermal barrier coatings  
TEM = transmission electron microscopy  
TI = transmitted impulse  
TQM = total quality management

TRIR = time resolved infrared radiometry  
TTBCs = thick TBCs  
TTT = temperature-time-transformation (diagram)  
ULSI = ultra large scale integration  
UPS = underwater plasma spraying  
UTS = ultimate tensile strength  
VPS = vacuum plasma spraying  
Y-PSZ = yttria-partially stabilized zirconia