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WILEY-VCH

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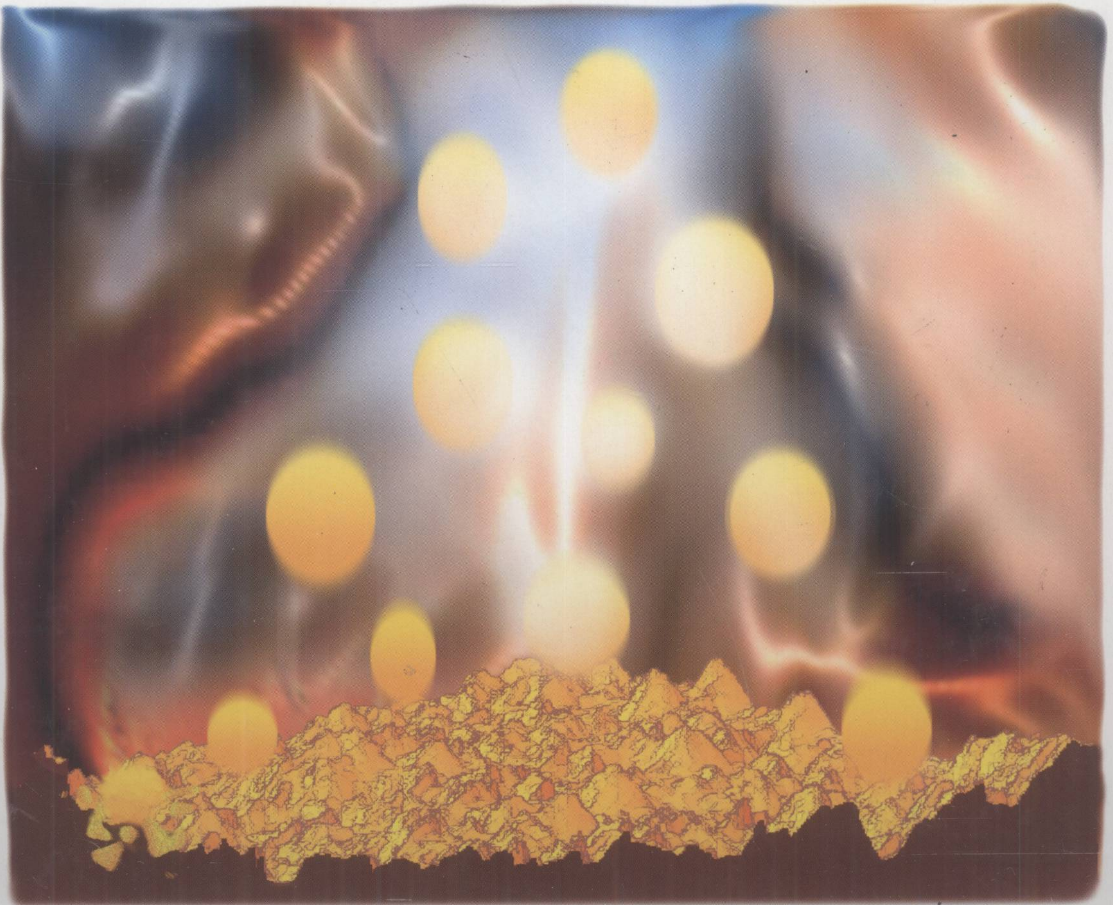
Principles and Applications

Second, Completely Revised and Enlarged Edition



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WILEY-VCH Verlag GmbH & Co. KGaA

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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Typesetting Thomson Digital, Noida, India
Printing betz-druck GmbH, Darmstadt
Binding Litges & Dopf Buchbinderei GmbH, Heppenheim

Printed in the Federal Republic of Germany
Printed on acid-free paper

ISBN: 978-3-527-32050-9

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2006

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Preface

Much work has been accomplished in the field of plasma spraying since this treatise first appeared in 1996. Since then the author and his research group at the Department of Mineralogy, Technische Universität Bergakademie Freiberg have conducted a series of studies on biomedical coatings, hard coatings based on TiC, protective mullite coatings for space-bound structures, photocatalytic coating based on titania and novel silicon nitride-based coatings for a variety of applications. This work has been prominently included in the new edition.

New substantial achievements in the field of modeling and numerical simulation of plasma spraying have prompted the author to collect the information scattered throughout the text of the first edition to form a new Chapter 6 by adding recent work in this area that is supposed to reflect the move from a more pragmatic, while still experimentally-based, approach towards theoretical approaches to support development of coatings purposely designed for ever-broadening areas of industrial applications. I owe much of this information to Professors Javad Mostaghimi (University of Toronto) and Sanjay Sampath (State University of New York, Stony Brook). Knowledge-based stochastic approaches to coating design such as artificial neuronal network analysis and fuzzy logic control have been included in the text and examples of their analytical power are given.

Information on suspension plasma spraying (SPS) and thermal plasma chemical vapor deposition (TPCVD) has been added to the text as well as several case studies to elucidate the advantages of these novel techniques. Also, a more in-depth account has been given on the explosively developing field of bioceramic coatings for implants designed to augment or replace damaged or missing tissue and body parts. Some results of high-velocity oxyfuel (HVOF) and cold dynamic gas (CDG) spraying, while not subject of this treatise, have been included occasionally to contrast the advantages or disadvantages of these techniques with those of atmospheric plasma spraying *per se*.

Furthermore, some misconceptions have been removed, typographical errors omitted, and a host of recent references, and new or revised figures added. However, the vast amount of information published during the last few decades in the field of thermal spraying cannot be accounted for in their totality. Alas, the resigned

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

ISBN: 978-3-527-32050-9

comment by the German poet Johann Wolfgang von Goethe relating to his autobiography "Out of my Life: Poetry and Truth" applies: "Such (. . .) work will never be finished; one has to declare it finished when one has done the utmost in terms of time and circumstances".

I am thankful to Gabriele whose love, deep understanding and enthusiastic support have been my guiding lights through many a dark day in the past years. Wiley-VCH Weinheim provided much support and encouragement during preparation of the text of this book. I am particularly indebted to Dr. Rainer Münz for his advice and constant help.

And yes, my musical taste has not changed since. I am still much devoted to the ancient Italian masters and their inspiring music.

Robert Heimann
Hann. Münden, November 2007

Preface to the First Edition

Thermal spraying encompasses a variety of apparently simple surface engineering processes by which solid material (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, a layer whose various functions include protection against wear, erosion, corrosion, and thermal or chemical degradation but also impart special electrical, optical, magnetic or decorative properties to the substrate/coating system. Also, thick coatings are applied in many industrial areas to restore or attain desired workpiece dimensions and specifications.

The text has been written with the theoretical and practical requirements in mind of students of materials engineering and materials science. It emerged from a nucleus that contained the topics presented to classes of Master students of the Materials Engineering Programme 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 gleaned experience in plasma spray technology during his work from 1987–1988 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 1988–1993 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 that 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

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

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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, the Verlag Chemie Weinheim, represented by Frau Dr. Ute Anton, supported and encouraged me in the endeavor to complete the manuscript in time. In this I failed miserably, though. Special thanks are due to Tommaso Albinoni and Antonio Vivaldi.

Robert Heimann
Freiberg, March 1996

Synopsis

Atmospheric Plasma Spraying (APS) – A Brief Account of the Underlying Physics

This synopsis provides a concise summary of the basic physics of plasma spraying, aimed to initiate the novice in the underlying principles of one of the most versatile materials processing technologies. The different aspects of the connected energy transfer processes and the interaction of powder particles with the plasma jet and the substrate to be coated will be treated in much more detail in the remainder of the book.

Plasma spraying is a rapid solidification technology during which material introduced into a plasma jet is melted and propelled against a surface to be coated. This technology is versatile: any thermally reasonably stable metallic, ceramic or even polymeric material with a well-defined melting point can be coated onto nearly any surface. However, in practice many limitations persist related to high coating porosity, insufficient adhesion to the substrate, occurrence of residual coating stresses, and line-of-sight technology.

Plasma spraying can be conveniently described as a connected energy transfer process, starting with the transfer of energy from an electric potential field to a suitable gas forming a plasma by ionization, proceeding with the transfer of thermal energy and impulse (heat and momentum transfer) from the plasma to the injected powder particles, and concluding with the transfer of thermal and kinetic energy from the molten or semimolten particles to the substrate to be coated.

The mode of injection of powder particles into the plasma jet depends on the grain size, the melting temperature and the thermal stability of the powder material. In general, injection can be done perpendicularly to the jet at its point of exit from the anode nozzle of the plasmatron (plasma 'torch'), in upstream or downstream mode at an angle to the jet axis, directly into the nozzle, or coaxially through a bore in the cathode. Upstream injection is used when increased residence time of the powder particles in the jet is required, that is when spraying high refractory materials. Downstream injection protects a powder with a low melting point from decomposition and vaporization, respectively.

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The plasma originates from ionization in an electric potential field of a suitable gas, preferentially argon or nitrogen. Hence a plasma by definition consists of positively charged ions and electrons, but also neutral gas atoms and photons. Moving charges within the plasma column induce a magnetic field $\boldsymbol{B}$ perpendicular to the direction of the electric field characterized by the current $\boldsymbol{j}$. The vector cross-product of the current and the magnetic field, $[\boldsymbol{j} \times \boldsymbol{B}]$ is the magneto-hydrodynamic Lorentz force whose vector is mutually perpendicular to $\boldsymbol{j}$ and $\boldsymbol{B}$. Hence an inward moving force is created that constricts the plasma jet by the so-called *magnetic* or *z-pinch* (Cap, 1984; Goldston and Rutherford, 1997). In addition to the magnetic pinch there is a *thermal pinch* that stems from reduction of the conductivity of the plasma gas at the cooled inner wall of the anode nozzle leading to an increase in current density at the center of the jet. Consequently the charged plasma tends to concentrate along the central axis of the plasmatron thereby confining the jet. As the result of these two effects the pressure in the plasma core increases drastically and the jet is blown out of the anode nozzle of the plasmatron with supersonic velocity.

A portion of this supersonic velocity will be transferred to the injected powder particles, that is, the powder particles will gain acceleration from the plasma jet by momentum transfer. The particle acceleration dV_p/dt is proportional to the viscous drag coefficient C_D and the velocity gradient between the gas velocity and the particle velocity, $V_g - V_p$, and inversely proportional to the particle diameter d_p and the particle density ρ_p as expressed by the Basset–Boussinesq–Oseen (BBO) equation of motion:

$$dV_p/dt = [3C_D \times \rho_g/4d_p \times \rho_p] \times (V_g - V_p)|V_g - V_p|,$$

where $C_D = 2[F_D/A_p]/[\rho_g \times u_R^2]$ with F_D Stokesian drag force, A_p cross-sectional area of the particle, ρ_g gas density, and $u_R = V_g - V_p$. Since C_D is also inversely proportional to the Reynolds number **Re** the numerical value of the latter determines the flow regime in the plasma jet, that is, laminar or turbulent flow. Most atmospheric plasmas jets are turbulent, that is, characterized by a nonsteady flow field around the immersed particles and thus a rapid change of the particle Reynolds number with time. Together with the problem of arc root fluctuation this turbulence introduces nonlinearity to the process (see below).

A large part of the (electric) energy spent on ionization of the plasma gas will be recovered by recombination in the form of heat, and the powder particles accelerated by momentum transfer along a trajectory in the jet will be heated by the hot plasma. The amount of heat a particle acquires can be approximated by the balance of the amounts of heat gained by convective energy transfer, $Q_C = h\,A\,(T_\infty - T_s)$ and of heat lost by radiative energy transfer, $Q_R = \sigma \cdot \varepsilon \cdot A \cdot (T_s^4 - T_a^4)$ with h = convective heat transfer coefficient, A = surface area of the particle, T_∞ = free-stream plasma temperature, T_s = particle surface temperature, T_a = temperature of the surrounding atmosphere, σ = Stefan–Boltzmann coefficient, and ε = particle emissivity. The heat transfer coefficient between a fluid and a (spherical) particle is frequently expressed by the Ranz–Marshall equation (Ranz and Marshall, 1952) as a function of the non-dimensional Nusselt number, **Nu**:

$$\mathbf{Nu} = 2.0 + b\mathbf{Re}^m\mathbf{Pr}^n$$

where **Re** = Reynolds number and **Pr** = Prandtl number. The coefficient b and the exponents n and m vary widely depending on the plasma conditions. In the original Ranz–Marshall equation m and n were set to be 0.5 and 0.33, respectively. To completely melt a (refractory) particle a certain degree of superheating is required, that is, the temperature of the particle has to be raised sufficiently high beyond the melting temperature to account for limited heat conduction within the particle, radiative energy losses and other more complex effects stemming from the nonlinearity of the process. Also, the viscosity of the liquid droplet has to be low enough to flow easily on impact with the substrate and hence facilitate proper bonding with its roughened surface. The degree of superheating depends on the Biot number, **Bi** that in this application is defined as the ratio of the thermal conductivity of the plasma gas, k_g to the thermal conductivity of the particle k_p, $\mathbf{Bi} = k_g/k_p$. For a particle to have a uniform temperature $\mathbf{Bi} < 0.01$ holds. The Biot number can be adjusted by selecting appropriate auxiliary plasma gases such as hydrogen or helium with increased thermal conductivities and specific heats that will increase the heat transfer rates from plasma gas to particles.

Finally, the more or less liquid droplet will impact the surface to be coated and, given a low enough viscosity, splash across the already deposited and frozen splats whose roughness determine to a large extent the solidification kinetics as well as the size and morphology of the newly arriving particles (Ghafouri-Azar *et al.*, 2004; Raessi *et al.*, 2005). The electron micrograph (Figure S.1) shows the surface of an APS hydroxyapatite coating with the typical overlapping particle splats as well as some apparently incompletely melted quasi-spherical particles that cling loosely to the surface.

The selection of the proper intrinsic (plasma power, argon gas flow rate, auxiliary gas flow rate, powder carrier gas flow rate *etc.*) and extrinsic (spray distance, powder feed rate, powder grain size, particle morphology, surface roughness *etc.*) plasma parameters is crucial for sufficient powder particle heating, flow and surface wetting on impact, and hence development of the desired coating porosity and adhesion to the substrate. However, overheating leads to an 'exploded' splat configuration with

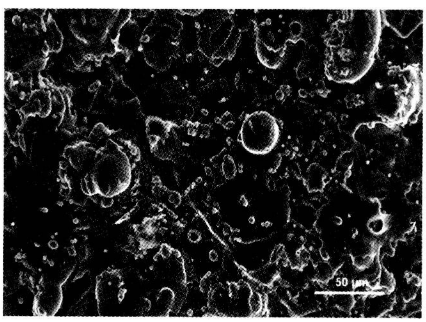

Figure S.1 Characteristic surface features of a typical APS hydroxyapatite coating with well-developed, overlapping particle splats and some loosely adhering incompletely melted particles.

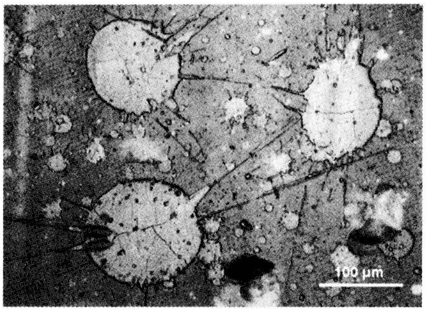

Figure S.2 Frozen-in-time traces of superheated 'exploded' alumina splats with material ejected on impact with a solid surface (Heimann, 1991).

increased microporosity, high residual stresses, and consequently reduced adhesion strength of the coatings as shown in Figure S.2.

The heat transfer from the molten particle to the solid substrate follows the generalized heat transfer relation expressed by the simplified Fourier equation

$$\text{div grad}\,\Theta - (1/a)(\partial\Theta/\partial t) = 0,$$

where Θ = temperature, a = thermal diffusivity, and t = time. The kinetic energy acquired by the particle will cause the splat to deform on impact thereby creating a shock wave moving with supersonic speed into the solid substrate. The ratio of deformation (flattening or spreading ratio) $\xi = D/d$ (D = splat diameter, d = original particle diameter during flight) depends on many parameters. Under simplifying assumptions the flattening ratio can be estimated using the semiquantitative Madejski splat-quench solidification model $\xi = D/d = A \times (\rho \times v/\mu)^z \approx \mathbf{Re}^z$, with **Re** = Reynolds number, ρ = density, v = impact velocity, and μ = viscosity of the melt. Many values for the pre-exponential coefficient A and the exponent z have been proposed in the literature, for example A = 1.2941, z = 0.2 (Madejski, 1976); A = 0.5, z = 0.25 (Pasandideh-Fard and Mostaghimi, 1996); A = 0.82, z = 0.2 (Watanabe *et al.*, 1992); A = 0.5, z = 0.25 (Hadjiconstantinou, 1999) or more recently, A = 0.925, z = 0.2 (Dyshlovenko *et al.*, 2006).

While in a dilute situation, with low-plasma loading conditions, particle movement, momentum and heat transfer can be considered a ballistic process without particle interaction, dense loading conditions appear to drastically change both the flow and temperature fields in a plasma jet. As such dense loading conditions are in practice selected for economic reasons during industrial plasma spraying, the impact of high powder feed rates on melting and spreading behavior of the particles must be considered. With increasing powder feed rates both momentum and temperature of the plasma will decrease for three reasons. First, the heat extracted from the plasma to melt a large mass of powder causes substantial local cooling of the plasma. Second, the evaporated fraction of powder can drastically alter the thermophysical, thermodynamic and transport properties of the plasma gas. Third, small powder particles with high optical emissivities evaporate easily and radiate away substantial amounts of plasma energy.

Larger rigid particles or the solidified part of an impacting particle can shatter on collision with the substrate surface owing to differential pressures across the particle as the leading and the trailing faces are subject to different dynamic pressures $p_{dyn} \approx C_D \times \rho_p \times v^2/2$. When the dynamic pressure exceeds the yield strength of the solid material fragmentation occurs. However, fragmentation is not confined to particle impact. Using fractal analysis it has been concluded that fragmentation may already occur in-flight along the particle trajectory when large thermal stresses develop owing to limited thermal conductivity within the particle (Reisel and Heimann, 2004).

Selection of the correct numerical non-dimensional parameters **Re, Nu, Pr, We, St** and **Bi** allows the process of plasma spraying to be modeled making somewhat simplified assumptions that have to satisfy the four general plasma conservation equations, that is, the continuity equation of mass conservation, the nonlinear Navier–Stokes equation of momentum conservation, the energy conservation equation and the species conservation equation as well as the Maxwell electromagnetic field equations (see for example Proulx *et al.*, 1985; Mostaghimi *et al.*, 2003; Ghafouri-Azar *et al.*, 2003; Raessi and Mostaghimi, 2005; also Dyshlovenko *et al.*, 2006).

It is a fact well known to the plasma spraying community that the properties can vary widely from coating to coating even though the spray parameters have supposedly been set within narrow ranges using sophisticated microprocessor-controlled metering devices and stringent quality control measures including intelligent statistical process control (iSPC), Taguchi methodology and the like. As it turns out, infinitesimally small changes of the input parameters will cause large, and in general nondeterministic changes of the output parameters and hence the properties of the coatings and their performance in service. Such behavior signals nonlinearity that arises from electromagnetic and magneto-hydrodynamic turbulences that affect the local magnetic field strength $\boldsymbol{B}$ and the electric current density $\boldsymbol{j}$, and hence the Lorentz force $[\boldsymbol{j} \times \boldsymbol{B}]$. The Lorentz force fluctuates rapidly with frequencies that are on the order of the residence time of the particles in the jet. In lockstep with the Lorentz force the plasma compression, that is, the z pinch changes and hence the rate with which turbulent eddies of cool air surrounding the plasma column are being entrained by the pumping action of the plasma. This alters the temperature distribution within the turbulent plasma jet dramatically and instantaneously so that the local thermal equilibrium breaks down on a scale that is small compared to the overall volume of the plasma. Then the system enters the realm of a heat transfer catastrophy of co-dimension 2, that is, a Riemann–Hugoniot (cusp) catastrophy (Thom, 1975). Since such nondeterministic behavior cannot be properly controlled by even the most stringent quality control measures plasma spraying is still by and large an experimental technique based on trial-and-error methodology and thus relies heavily on experience and expert knowledge.

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Contents

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ISBN: 978-3-527-32050-9