Thermally sprayed bio-ceramic coatings : a study on process parameters influence on coating properties

Cizek, Jan

2010

Cizek, J. (2010). Thermally sprayed bio-ceramic coatings: a study on process parameters influence on coating properties. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/47238>

<https://doi.org/10.32657/10356/47238>

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THERMALLY SPRAYED BIO-CERAMIC COATINGS: A STUDY ON PROCESS PARAMETERS INFLUENCE ON COATING PROPERTIES

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2010

THERMALLY SPRAYED BIO-CERAMIC COATINGS: A STUDY ON PROCESS PARAMETERS INFLUENCE ON COATING PROPERTIES

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**SCHOOL OF
MECHANICAL AND AEROSPACE ENGINEERING**

A postgraduate research project
presented to the

Nanyang Technological University

In fulfillment of the requirements for the Degree of
Doctor of Philosophy

March 2010

ABSTRACT

The surface is a crucial part of a biomaterial in direct contact with organic tissues and body fluids. Often, the quality and durability of surfaces are decisive factors for the overall performance and reliability of the biomaterial components. For enhancement of the surface properties, cost-effective and reliable thermal spray techniques are used.

The present research relates to thermal spraying of bio-active ceramic coatings. Reliable atmospheric plasma spray and innovative cold spray techniques were employed for coating deposition. Two different materials were used in this study: hydroxyapatite (HA), a well-established calcium phosphate ceramic material, and titanium dioxide (TiO_2), a promising novel substitute for some conventional biomaterials. Wet chemical synthesis was used to produce pure hydroxyapatite powder. The powder was calcined (1273 K for 120 mins) and sieved (32 – 45 μm). Fused TiO_2 powder customized for atmospheric plasma spray was heat treated at 1023 K for 120 mins and sieved.

Two focal points of this research work were: a) the changes in powder particles in-flight properties within the spray process due to the influence of various spraying parameters; and b) the changes in resulting coating properties due to changes in the in-flight properties

For the plasma spray technique, the investigated parameters were the system net power, main, auxiliary and carrier gas flows, powder hopper feeder system revolutions per minute and spray distance. For the cold spray system, the parameters studied included electric current, process temperature, main gas and feeder gas pressures, and substrate materials.

To determine the in-flight powder particle properties, fast-shutter diagnostics camera equipped with a laser illumination system was employed. In-situ temperature and velocity profiles of sprayed powder particles were scanned and recorded at different distances from the gun. To assess powder particles in-flight properties, two different experimental approaches were introduced. One-at-a-Time technique (OAAT) investigated the influences of the six spraying factors. The average temperatures and velocities of particles were measured as 2312 – 2674 K (201 – 341 ms^{-1}) for HA and 2121 – 2621 K (158 – 243 ms^{-1}) for TiO_2 . Spray distance was found to be the dominant factor for HA while net power and spray distance factor were found to have equally strong effect on the in-flight properties of TiO_2 particles. Carrier gas

phenomenon was observed. Taguchi design allowed several trends different from OAAT method results. Basic factors relative importance within measured ranges was introduced. It was found that particles temperature was dominantly governed by spray distance factor (45% vs. 36% influence for HA and TiO₂, respectively) and net power (24% vs. 26%). Velocity of HA particles was found to be controlled by spray distance (33%) and main gas flow (24%), while for TiO₂ powder the net power (48%) is the most dominant factor. Several major factors interactions were revealed, e.g. net power & main gas flow. Analysis of variance method was introduced: net power, main gas flow and spray distance parameters proved to have an effect on HA particles at highest confidence level (99%) while TiO₂ powder was proven to be influenced by all factors except for auxiliary gas flow. Regression analysis of experimental data was carried out. Factors dependence types were determined (predominantly linear and quadratic) and notations of obtained relations were introduced.

Six different combinations of parameters (leading to high/moderate/low in-flight temperatures/velocities) were selected for plasma sprayed coatings production while six preset combinations were used for cold spray technology.

Surface roughness of the samples was determined to vary from $R_a = 7.41 - 19.39 \mu\text{m}$ for HA and $R_a = 4.80 - 7.15 \mu\text{m}$ for TiO₂ and to be substantially lower for cold sprayed samples ($R_a = 1.33 - 3.23 \mu\text{m}$). Phase and element analysis of the coatings (Rietveld analysis of XRD patterns and EDX spectra measurements) confirmed that the phase composition of both coatings differ from original powder feedstock considerably (e.g. increase of CaO content in HA from 0.5% up to 26%, anatase content increase from 4% up to 13% in TiO₂). Cold spray deposition was proven to be less susceptible to phase composition changes. SEM technique was employed for coatings morphology characterization (top-layer and cross-section).

Tensile adhesion test (ASTM C-633) was performed on the plasma sprayed coatings, demonstrating superior adhesion values of TiO₂ (10.95 MPa) over those of HA (6.16 MPa). Coating micro-hardness was measured (0.06 - 1.16 GPa for HA and 0.16 - 0.73 GPa for TiO₂) as well as coatings elastic moduli (13 - 27 GPa for HA and 32 - 70 GPa for TiO₂). Porosity of the coatings was specified to vary from 7 - 28% for HA and 6 - 28% for TiO₂ coatings, respectively.

Abstract

Two additional sets of experiments were conducted. Fatigue life determination of plasma sprayed specimens specified enhancement of lifespan of coated samples as compared to non-coated bodies (increase of up to 41% for HA and up to 46% for TiO_2 specimens). Experiments on single splats collection onto polished surfaces allowed studying the spreading behavior of particles upon impacting a substrate.

Software simulations and computations were performed to complete the coatings analyses. In-flight powder properties were simulated using Jets&Poudres numerical code, in disagreement with measured values (difference up to 40%). Coating deposition process was simulated using Simulent-Coat code, providing average values of deposition efficiency, coating porosity and surface roughness ($R_a = 6.74 - 12.09 \mu\text{m}$ for HA and $R_a = 4.85 - 14.46 \mu\text{m}$ for TiO_2). Impacts of individual splats onto substrates were simulated using Simulent-Drop software and morphology of splats was compared with experimentally obtained results.

ACKNOWLEDGEMENTS

I would like to express my utmost gratitude to all people who helped me during the entire period of my PhD candidature. Whether it was supervising of the entire work, assistance with carrying out the experiments, guidance in evaluating the results, advices on composing the thesis or even moral support when things went wrong, finishing this project would have never been possible without every single one of you. Thank all of you so much.

Nevertheless, there are several names which deserve to be mentioned separately:

First of all, my very special thanks go to *Prof. Khiam Aik KHOR*. Apart from all the burdensome supervising, you also were a good friend to talk to during bad times and proved amazing ability to put me back onto my feet. Thank you so much, Michael. Hope our friendship will last wherever our steps will bring either of us.

Likewise, I'd like to thank another person who did a lot during the process of this study composition, *doc. Jan SIEGL*. For all your patience. For surviving me and remaining sane. For all your help out of the school walls. Dekuju, Honzi.

I would also like all the schoolmates around me to know I sincerely appreciate all their help and value the friendship we have. For all, *Monts, Seb, Jinling* and *Ligen* have to be mentioned for all the school / out of school support and help they provided me with.

Furthermore, I wouldn't want to omit to thank all the people who had made things run smoothly hardware-wise, the technicians: ladies *Sandy, Mei Yoke, Shiau Kee* and gentlemen *Koh Soon Hong, Chang Set Chiang, Leong Kwok Phui, Sad'on, Thomas* and *Sam* from Ceramics Lab.

And last, but definitely not least, *my family members and friends*, the people supporting me all the time, whether from Asia, Europe or wherever. Particular thanks are, I believe, not in order, you all know. My sincere thanks go to every single one of you...

DEDICATION

...to my parents

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NOMENCLATURE

Abbreviations

316L/SS	Stainless steel 316L
AGF	Auxiliary gas flow (plasma spray)
AISM	Active image spray monitoring
ANOVA	Analysis of variance
APS	Atmospheric plasma spray
CAPS	Controlled atmosphere plasma spray
CCD	Charge-coupled device (CCD chip)
CGF	Carrier gas flow
CMP	Calcium metaphosphate
CNC	Computer numerical controlled
CPP	Calcium pyrophosphate
CPPD	Calcium pyrophosphate dihydrate
CS	Cold spray
CSP	Cold spray parameters
DC	Direct current
DCP	Dicalcium phosphate
DCPD	Dicalcium phosphate dihydrate
DOE	Design of experiments
DOF	Degrees of freedom
EDX	Energy-dispersive X-ray spectroscopy
ePTFE	Expanded poly(tetrafluoro ethylene)
FEM	Finite element method
GOF	Goodness of fit
GPM	Grams per minute, a feeding mode in plasma spray
HA	Hydroxyapatite
HCP	Heptacalcium phosphate
HVOF	High velocity oxy-fuel spraying
ICP	Inductively coupled plasma
MCPM	Monocalcium phosphate monohydrate
MGF	Main gas flow (plasma spray)
MIP	Mercury intrusion porosimetry
NOP	Number of passes (cold spray)
NPW	Net power level (plasma spray)
OAAT	One-at-a-Time experimental method
OCP	Octacalcium phosphate
OHA	Oxyapatite
PDO	Poly(p-dioxanone)
PET	Poly(ethylene terephthalate)
PFG	Pressure of feeder gas (cold spray)
PGA	Poly(glycolide)
PISM	Passive image spray monitoring
PIV	Particle image velocimetry
PLA	Poly(lactide)
PMMA	Poly(methyl methacrylate)
PS	Atmospheric plasma spray
PSP	Plasma spray parameters
PTFE	Poly(tetra fluoroethylene)
PTMC	Poly(trimethylene carbonate)

Nomenclature

PUR	Poly(urethane)
PVC	Poly(vinyl chloride)
PWG	Pressure of working gas (cold spray)
RF	Radio frequency plasma
RPM	Powder hopper revolutions per minute
SEM	Scanning electron microscopy
SI	International system of units
SPR	Spray (stand-off) distance (plasma spray)
TBC	Thermal barrier coating
TCP	Tricalcium phosphate
TDHP	Tetracalcium dihydrogen phosphate
TEM	Transmission electron microscopy
TiO ₂	Titanium dioxide
TPG	Temperature of pressure gas
TTCP	Tetracalcium phosphate
UHMWPE	Ultra-high molecular weight poly(ethylene)
VOF	Volume of fluid calculation method
XRD	X-ray diffraction

Symbols

α_c, α_s	Thermal expansion coefficient of a coating or substrate
c_p	Specific heat of the gas at constant pressure
c_v	Specific heat of the gas at constant volume
k	Isentropic expansion factor (cold spray, $k = c_p/c_v$)
m_a	Molecular weight (molar mass)
P	Inlet gas pressure (cold spray)
P_e	Exhaust gas pressure (cold spray)
R	Ideal gas constant (8.314 Jmol ⁻¹ K ⁻¹)
R_f	Relative fatigue life
T	Absolute temperature (general notation)
v	Velocity (general notation)

SCOPE

The presented thesis is divided into *four apparent parts* comprising *nine chapters*.

First part (chapters I, II and III) introduces the reader to the theoretical background of the thesis and the general objectives covered. In *Chapter I*, the *objectives of this study* and motives for the work realization are explained. In the following *Chapter II*, a *literature review* of state-of-the-art of thermal deposition techniques is presented, focusing on the two methodologies used in this work - atmospheric plasma spray and its younger counterpart, cold spray process. Some general issues of thermal spray processes are addressed and a summary of advantages and possible problematic areas is discussed with respect to the experimental work carried out within the scope of this research. Second part of the literature review is devoted to the problems of biomaterials, an upcoming, fast-growing scientific area of a paramount importance. The emphasis of this part of the thesis is put on the problems of hard tissue bioimplants and description of the problems related to this area. *Chapter III* presents the *experimental setup* used for the purposes of this study. It provides a detailed description of the devices used, estimating particular systems stability and relative results reliability. Experimental methodology concept is described in detail and statistical processing of the results is explained. Two major experimental approaches for powder particle in-flight properties measurement are introduced. Furthermore, software code calculations are summarized and their implementation is given in detail. *Second part* of the thesis is covered in *Chapter IV: Powder feedstock*. The powders used for the purposes of this study are introduced, their modifications and processing is described and powder properties characterization methods are given in detail. A summary of all experimental results is presented in the *third part* of the thesis along with respective results discussion. *Chapter V* presents the results of powder particles *in-flight properties* measurements. Regression analysis of the results is then employed and plasma spray process governing equations are constructed. Results of various *coating properties* are demonstrated in *Chapter VI*. Coating hardness, porosity, adhesion, surface roughness results are provided and results of XRD, EDX and SEM analyses are summarized. Results of *additional measurements* are provided in *Chapter VII*.

Novel fatigue life measurements are described and the coatings influence on specimen fatigue lives is determined. Collection of single splats on polished substrates is described in detail. All obtained results are compared with supportive software simulations. *Fourth part* of the thesis introduces extended *discussion* of the obtained results in *Chapter VIII* and major *conclusions* are drawn in *Chapter IX*.

The following flowchart is provided to simplify reader’s orientation in the thesis concept:

CHAPTER 1: OBJECTIVES OF THE STUDY

In this introductory chapter, motivation for realization of presented research is given, the main aims of the work are described and the possible work contribution is discussed.

1.1 Motivation

One of the fastest growing research areas of contemporary science is the problem of *biomaterials research, development and application*. This research area, combining interdisciplinary approach of state-of-the-art materials engineering and innovative biomedical research, gained particular importance during the last two decades.

Spanning the areas of materials preparation (novel materials development, possible utilization areas, traditional materials improvements, various methods of final products production), its applications (of both surgical and non-surgical nature) and post-treatment investigation (acceptance in living tissues, long-term service life applications evaluation, in-vivo investigations feedback for further materials development), biomaterials have become one of the top-notch focal points of nowadays materials science.

One of the recognized biomaterials applications section are the *hard tissue replacements*. Utilization of present-day technologies along with the usage of modern, novel materials facilitate the production of increasingly reliable orthopedic implants of superior properties. Acquired research results and knowledge enable the surgeons to treat the problems of pain relief and restoration of mobility and/or functionality in case of various partial- or full-scale joint prostheses (knees, shoulders, ankles, elbows, wrists, hips) or mineralized tissues (bones, dental implants) more effectively and with higher success ratio.

Considering various aspects, a crucial part of every hard-tissue implant is its *surface*. The properties of every implant's surface are of vital importance for e.g. prosthesis integration and acceptance in tissues, its reliability or overall lifetime performance. The need for production of top-quality implants has therefore led to an increased attention in the areas of designing, optimization and modifications of implant surfaces.

One of the major groups of techniques for enhancement of materials surface properties is *thermal spraying*. This category of materials' properties modifications consists in deposition of a protective layer of special-purpose material (coating) onto the body fabricated from

primary, usually performance providing material (substrate). Considerable number of potential applications of thermal spray methods involves, among others, modifications of biomaterials surfaces.

Extensive research and thorough investigations in recent years have helped to broaden our understanding of some key principles and fundamental knowledge on the characteristics, functionality and properties of coatings deposited onto biomaterial implants surfaces (e.g. various publications by Khor, Berndt and Gross [1-14]) and provided an important data for different parts of biomaterials surface modifications using various thermal spray processes.

However, the results of previous research work mostly consist of fragmented scientific findings with limited interconnection to the overall scope and there still is a serious lack of a systematic research on this topic. Also, certain views on the thermal spray technology are based on overall acceptance of general tenets not supported and verified by a proper research. Furthermore, in spite of the fact that the process of biomaterials surface coating deposition plays a crucial role for the implants success, there are still parts of the technology not-fully understood or areas partly unexplored.

A systematic research on the process of thermal spraying of biomaterials encompassing all stages of layer deposition together with the need of proper investigation of partly unexplored or unclear areas of this technology, as well as the idea of validating and/or denial of certain traditional views on the process itself were the basic motives for realization of this research work project.

1.2 Research Aims

The general purpose of this study is to successively cover *two main stages* of the thermal deposition process: *the influence of selected thermal spray parameters on the in-flight properties of the deposited biomaterial*, particularly its in-situ temperature and velocity and to evaluate *their influence on some characteristics and properties of resulting coatings* vital from the point of view of applications in hard-tissue replacements.

Two different technological processes were used in this study, *atmospheric plasma spray* (APS, PS) and innovative *cold spray* method (CS). Two bioactive materials in form of a

Objectives of the Study

powder were used to carry out the experiments: *hydroxyapatite* (HA) and *titanium dioxide* (TiO₂).

Four *fundamental topics of the experimental work covered within this study* are:

1. To observe the conditions to which the powders are exposed to during their spraying and to investigate the influence of selected system parameters on powder particles in-flight temperature and velocity
2. To determine the influence of powder particles temperature and impact velocity on selected coating properties
3. To compare influence of two different thermal spray technologies (namely atmospheric plasma spray and cold spray) on selected coating properties
4. To understand mutual interrelationship of the various measured coating properties (including single splats shape and morphology) and particles in-flight properties during coatings deposition

CHAPTER 2: LITERATURE REVIEW

This chapter is divided into two main parts. The first part provides a general summary of the *thermal spray technology*. It describes the essentials of the process of thermal deposition of materials followed by a more detailed description of individual thermal spray technologies commonly used. Emphasis is put on atmospheric plasma spray and cold spray processes as the techniques used in this study. An introductory overview of some general issues encountered in the process of thermal spray deposition of materials is summarized with respect to the research aims of this project. Second part of the literature review is devoted to the problems of *biomaterials*. A general overview of the topic of biomaterials is briefly described. To facilitate easier orientation in biomaterials terminology, a basic order in biomaterials taxonomy is provided along with present-day biomaterials application examples. Furthermore, a summary of current biomaterials is listed and special sub-chapters are devoted to the properties of hydroxyapatite and titanium dioxide as the two materials used in this study.

In recent years, the properties of common and traditional materials like wood, steels or clay-based ceramics became insufficient to supply the needs of current materials engineering requirements. Driven by the needs for lighter, stronger, stiffer, tougher, fatigue or environment resistant or human tissue compatible materials, the market demands superior, high-performance materials of unique properties tailored for particular uses. Such demand led to a birth of new-generation materials, like e.g. fiber reinforced metal matrix or polymer based composites, high-performance plastics, blended powders sintered ceramics, high-strength steels or superalloys.

Despite the rapid development of this new-generation materials, a production of materials able to withstand increased mechanical loading, high temperatures, chemical attacks or various degrading environmental factors still remains one of the most challenging topics in today's materials engineering. The problem of development of a suitable material becomes increasingly difficult in case of combination of several concurrent degrading factors (e.g. a high-pressurized piping of chemical waste treatment factory at periodically elevated temperatures). Some of the most frequently referred materials degrading factors are summarized for illustration [15-17].

- abrasion, wear, erosion or material fatigue (mechanical loading)

- general, pitting, crevice, galvanic or high temperature corrosion, oxidation, dealloying, aggressive chemical intrusion, stress corrosion cracking (chemical attacks)
- high temperature fatigue, thermal fatigue, creep or thermal shocks (thermal degradation)
- hydrogen embrittlement, radiation, body fluids and tissue activities, aging (environmental factors)

The most susceptible part of virtually any component from the point of view of failure is its surface, where majority of the degrading processes are initiated. To suppress the impact of these degradation processes, *tailored surface modifications and alterations* are often employed, e.g. changing the composition, microstructure or properties of the outermost surface layers by chemical, thermal, mechanical or combined processes or forming a special protective layer or coating on the surface of the component. A typical group of surface modification methods representing the coating deposition treatment is thermal spraying technology.

2.1 Thermal Spray Technology

In Switzerland about 1915, inventor Max Schoop found that by injecting metallic powder into hot gases formed by a combustion of oxygen and a fuel gas such as propane or acetylene, the heat-softened powder would adhere to the surface of a substrate to which the effluent had been directed. This flame spray coating process, known as metallizing, has been a standard method for applying metal coatings for several decades and has become a foundation stone of what is nowadays known as *thermal spray technologies*.

In the following years, novel methods and modifications of the thermal spray technology emerged, increasing the versatility while retaining its advantages over another deposition processes - relative ease of components fabrication and high cost-efficiency.

2.1.1 Thermal Deposition Fundamentals

The thermal spray is a group of processes in which finely divided metal or non-metal materials are deposited in a molten or semi-molten state onto a prepared substrate to form a spray deposit [18]. The *material is inserted in various forms, heated in gaseous medium and propelled towards the substrate surface* [19,20]. Depending on the technology, the high velocities of acting gases cause acceleration of the small particles of the material up to 1400 ms^{-1} [21]. Eventual heating can cause further increase in the particles kinetic energy and likely cause partial or full-scale melting of the particles [22]. The immense kinetic energies

stored in particles account for the large amount of both elastic and plastic deformation of the molten or semi-molten particles during the process of its *solidification at the surface*. The solidified particles are called *splats* and due to common concurrence of acting temperature and velocity, the resulting shape of such splats is far from ideal spheres, with their shape best described as lamellar [22-25]. Generally, the size of these solidified platelets ranges from few micrometers to over 100 micrometers in diameter and about 1 – 20 μm in thickness. Synchronous relative movement of the thermal spray source against the substrate enables covering the substrate in *individually deposited layers*, each consisting of millions of solidified splats. *Thermally sprayed coatings* consist of several layers and its typical thickness could vary from 5 μm (usually a single layer coating) to 10 mm (usually a coating with graded or sandwich layer structure).

In detail, *three distinctive phases can be distinguished in every thermal deposition process*. Their descriptions are expanded into following sections 2.1.1.1, 2.1.1.2 and 2.1.1.3.

2.1.1.1 Injection of material and its interaction with the surrounding atmosphere and acting gases

The material is inserted in various forms (wire, rod, powder, liquid suspension, etc.) in radial or axial direction to the thermal spray torch and propelled towards the substrate. The *total energy of the particles is increased* by means of the chemical energy of gas combustion, electrical energy and/or the energy of the acting gases and is partially transferred into heat, often resulting in *partial or full-scale melting* of the particles. For materials with high thermal conductivity and low boiling point, *evaporation* of material is likely to occur (Fig. 2-1).

The jet of semi- or fully-molten particles is surrounded by *air or controlled atmosphere*. (CAPS, Controlled Atmosphere Plasma Spraying [26-28]). Due to its different thermal dissociation energies, different types of the surrounding medium (e.g. argon, nitrogen) lead to different temperature gradient distributions in space and, consequently, different lengths of the jet [26]. The heat absorbed by a particle is directly proportional to the length of the jet.

The influence of *pressure within the spraying chamber* is apparent under direct observation of the jet. Generally, higher pressure values decrease the length of the jet [29]. However, incidence of chamber pressure on particles in-flight properties differs for different variants of thermal spray processes and no general conclusion can be made.

In special cases, the deposition is realized in fully evacuated chambers to e.g. prevent undesirable oxidation.

Fig. 2-1: Schematic of eventual interactions of material particle and thermal jet

Selection of the working gases (mono- vs. di-atomic, momentum vs. heat transferring) has a direct influence on the jet properties and is therefore of utmost importance to the energy transfer distribution. In general, use of diatomic gases (such as nitrogen, hydrogen) leads to lower temperature jets, higher noise production and increased equipment wear as compared to monatomic gases. Momentum transferring gases (e.g. argon) predominantly influence particles in-flight velocity while temperature transferring gases (e.g. helium) are more likely to have an impact on the amount of heat particles receive.

2.1.1.2 Interaction of the particle with the substrate surface and formation of splats

Certain important coating characteristics are particularly influenced by the properties of the first deposited layer (e.g. coating adhesion). The first layer of splats is in direct contact with substrate surface. To ensure the coating superior characteristics, adequate *surface preparation* is therefore necessary prior to thermal deposition process.

It was found that substrate *surface roughness* is a crucial factor influencing adhesion strength between materials, with substrates of higher roughness yielding higher bond strengths. On microscale, the surface roughness influences the substrate geometry, in particular the future contact area between substrate and impacting particle, facilitating the mechanism of *mechanical interlocking* and therefore changing the nature of the future bond (Fig. 2-2). Surface roughness can be altered by grit-blasting (increase in roughness) or shot-peening (less material removal) techniques.

Fig. 2-2: Schematics of mechanical interlocking of impacting particle due to substrate roughness

Another set of substrate properties affecting the contact with the first layer are the characteristics related to chemical composition of the substrate, especially purity of its surface and its wettability. To modify and alter such properties, *chemical modifications* are employed prior to thermal deposition, e.g. chemical cleaning, deliberate oxidation, degreasing or application of grease or oil contaminant films [30]. A thin *bond layer* (interlayer with good bonding properties with both substrate and coating) is frequently deposited onto a surface preliminary to the process of deposition of selected material to ensure more coherent and continual transition of properties.

The last type of substrate properties influencing coating quality are those of thermal nature, e.g. *substrate temperature* prior, during and after the spraying, its heat conductivity or coefficient of thermal expansion. The substrate temperature highly influences the behavior of a particle upon impact and the process of morphology and shape changes before its solidification [24,25,31-35]. A so-called *transition temperature* is the main factor inducing the particles shape changes. For a substrate with temperature below the transition temperature, a regular

disc-shaped splat is formed in the central part of the flattening particle while a noticeable *splat splashing* occurs at the periphery. For substrates above the threshold value, no splashing occurs and a regular disc-shaped splat is formed. Consequently, microstructure integrity is improved and number of properties is significantly enhanced (Fig. 2-3) [35,37-38].

Fig. 2-3: Effect of in-situ substrate temperature on morphology of solidifying particles [36]

The mechanism of this splat morphology change has been a subject of significant investigation importance. The causes can be attributed to a number of factors such as higher solidification rate at the low substrate temperature, poor wetting, a surface contamination at lower temperatures etc [38].

The influence of substrate's heat conductivity and coefficient of thermal expansion are closely associated with the topic of internal stresses within the deposited layers and will be discussed thoroughly in chapter 2.1.3.

In a typical thermal spray process, a sprayed particle has a relatively *high velocity and temperature* at the moment of its impingement at the surface. Upon impact, the particle undergoes *rapid cooling* (up to 10^6 Ks^{-1}) and its kinetic energy and accumulated heat are transformed into deformation energy (e.g. particle's flattening, spreading, shape deformation or

conformation and adherence to surface irregularities), particle solidification (liquid to solid state transformation, phase changes related to cooling, inherent stresses), underlying substrate or previous layers microscale melting and global composite heating.

Due to rapid quenching, *recrystallization* of grains occurs during particles solidification. The recrystallization character is a function of the temperature gradient and velocity of particle spreading upon impact. Three different solidification microstructures have been reported to develop: a planar microstructure in case of high temperature gradients or high interface velocities, a cellular microstructure for medium interface velocities and dendritic microstructure in case of low interface velocities or small temperature gradients. It is possible to distinguish these morphologies using phase composition experimental methods (3.2.2.3).

As the final quality of the entire coating is directly dependent on the mutual substrate-splat or splat-splat interactions, a single splat formation, its shape, morphology and spreading behavior is one of the most crucial aspects of thermal deposition process and would be studied in detail in the following text (3.2.3.2).

2.1.1.3 Coating build-up by stacking of splat layers

As the spray torch is moved over the surface in successive passes during the deposition process, a *coating* is created on the substrate material. Its *thickness* is influenced by a number of spray gun passes, relative speed of the gun towards the surface, the efficiency of the deposition process and material deposition rate (indicated in kgs^{-1} ; proportional to the number of particles entering the jet, usually tenths of millions particles per second [39]).

Layer by layer, the coating is built up, having its inimitable, messy structure consisting of solidified splats, unmolten or partly molten particles, voids and/or various impurities such as oxide occlusions (Fig. 2-4) [40-46].

Due to conditions to which the material is exposed to during thermal spray (e.g. elevated temperature, rapid solidification, plastic deformations), phase and structural changes, chemical decompositions, selective component evaporations, oxidation and other property changes occur frequently. Overall coating characteristics resulting from inherent coating microstructure and properties are directly related to the problems of some common issues encountered in thermal deposition process and will be described in detail in chapter 2.1.3.

Fig. 2-4: Characteristic structure features of thermally deposited coating

Virtually, any material can be used as long as it does not decompose, vaporize, sublime or dissociate prior to melting (the recommended difference between melting and decomposition or evaporation temperatures is preferably greater than 300 K) [47].

2.1.2 Deposition Techniques

Thermal spraying covers a range of techniques which differ in the process of heat generation and subsequent jet properties. A broad spectrum of applicable materials allows a production of coating of properties targeted for particular applications.

The main thermal spray techniques and their relative properties are summarized in Table 1. The variations in resulting coating properties are predominantly caused by the differences in the respective temperatures of generated jets and the velocities the particles are accelerated to. Fig. 2-5 graphically illustrates the temperature and velocity working ranges of the particular thermal spray processes.

Table 1: Main Thermal Spray Processes [47,48]

Deposition technique	Flame spraying	Electric arc spraying	Detonation gun	HVOF	Plasma spray	Cold spray
Heat source	$O_2 + H_2$ $O_2 + C_2H_2$ $O_2 + C_3H_6$	arc between electrodes	oxygen C_2H_2	$O_2 + H_2$ $O_2 + C_2H_2$ $O_2 + C_3H_6$ $O_2 + C_3H_8$ $O_2 + \text{kerosene}$	plasma arc	regular gas heating
Propellant	O_2	air	detonation shock waves	O_2	He, Ar	He, N_2 , air
Material feed type	powder wire rod	wire	powder	powder	powder	powder
Flame or plasma exit temperature [K]	2800 - 3300	4300 - 6300	4800	3000 - 3400	3000 - 16000	20 - 700
Typical particle velocity [ms^{-1}]	30 - 180	240	800 - 1000	800 - 1400	120 - 600	300 - 1200
Coating materials	metallic ceramic	ductile materials	metallic ceramic plastic	metallic ceramic	metallic ceramic plastic	metallic ceramic plastic
Bond strength [MPa]	20 - 28	40 - 60	> 70	40 - 96	10 - 70	40 - 300
Porosity [%]	10 - 25	8 - 15	0.5 - 6	0.1 - 2	2 - 20	0.1 - 3
Oxide content [%]	4 - 6	0.5 - 3	0.1	0.2	< 1.0	< 0.1
Particle injection mode	axial and perpendicular	at angle to jet	axial	axial	perpendicular	perpendicular
Flame length [cm]	< 10	< 15	< 10	< 10	< 15	< 10
Relative cost [\$]	3	1	10	5	5 - 10	7

Fig. 2-5: Temperature/velocity ranges of various thermal spray processes

Following sub-chapters provide details on flame spray, electric arc, detonation gun and HVOF processes as well as detailed characteristics of plasma spray and cold spray technologies as the two methods used in this study.

2.1.2.1 Flame Spray

In *flame spray* process (combustion spray, Fig. 2-6) [50-55], oxygen and a fuel gas such as hydrogen, acetylene or propylene are fed into a torch and ignited to create a flame. The chemical energy released from the combustion is used to heat the powder, rod, wire or liquid suspension and blow the molten particles onto the substrate. Flame spray is the oldest of the thermal spray processes and generally has a low cost.

As seen from Table 1, the flame spray technique has the lowest temperature (2800 K) and velocity of the processes with the exception of cold spray. It is therefore not recommended for use with materials requiring high temperatures to melt (e.g. tungsten, ceramics). Due to lower spraying velocities, the resultant coating has relatively high porosity. Flame sprayed coatings have relatively low bond and cohesive strengths.

Fig. 2-6: Schematic of the flame spray technique [49]

Flame spraying is used for e.g. protecting metal constructions or LPG cylinders against corrosion (Al or Zn coatings) or repairs of compressor cylinders (stainless steel coatings).

2.1.2.2 Electric Arc

In the *electric arc spray* process (wire arc spray, Fig. 2-7) [50-55] two wires are simultaneously brought into close contact with each other at the nozzle. A high-current

potential difference is applied on the wires and initiates an arc that melts the tips of the wires. Atomizing gas (usually compressed air), is used to strip the molten material off the wires and transport it towards the substrate.

Electric arc spray has the highest deposition rate of all thermal spray processes and can be used to spray large surface areas or employed in a flow production components spraying. The process is energy efficient since almost all of the energy input is used to melt the material and is reasonably expensive. The combination of relatively high temperature and slightly higher particle velocities gives wire arc sprayed coatings superior bond strengths and lower porosity levels as compared to flame sprayed coatings. However, the use of compressed air for droplet atomization and propulsion gives rise to high oxide content in the coating [51]. Also, the range of applicable materials is limited to electric conductors (usually stainless steels, Ni-Al alloys, Al, Zn, Hastelloys, bronzes).

Fig. 2-7: Schematic of the electric arc spray technique [49]

Typical use of electric arc spraying include reclamation of engineering components (bearings, shafts) using steels or bronzes or spraying electronic component housings with conductive coatings for shielding from electromagnetic interference.

2.1.2.3 Detonation Gun

A *detonation gun* (Fig. 2-8) [48,50,51,55-57] consists of a water cooled barrel and a spark plug mechanism. A controlled mixture of gases, usually oxygen and acetylene, is fed to the barrel with portion of a powder. A spark is used to ignite the gas and the resulting detonation

wave heats and accelerates the powder as it moves down the barrel. A pulse of nitrogen gas is used to purge the barrel after each detonation. The process is repeated up to 10x per second.

A combination of high temperature and supersonic velocity of particles gives rise to the smallest porosity amidst the thermal spray processes and high adhesion strengths between the coating and the substrate. Hardness of detonation gun sprayed coatings is among the highest. The detonation gun spraying is a non-continuous technique, often resulting in unevenness in the coating thicknesses. Excessive noise is generated during the deposition process [54].

Fig. 2-8: Schematic of the detonation gun technique

Detonation gun spray method is designed for applying hard materials (e.g. carbides) onto substrates subjected to aggressive wear.

2.1.2.4 HVOF

The most recent addition to the high-temperature thermal spray family is *High Velocity Oxy Fuel Spraying* (HVOF, Fig. 2-9) [41,47,50,51,54,55,58-61]. In this process a fuel gas such as hydrogen, acetylene, kerosene (a mixture of petroleum hydrocarbons C_9H_{20} - $C_{17}H_{36}$), propane or propylene are injected into the combustion chamber of the torch at high pressures and mixed with oxygen. The mixture is ignited and then exits through a small-diameter water-cooled barrel, generating a supersonic exhaust gas jet. Using carrier gas, the powder is injected laterally into the jet, accelerated and deposited.

The internal combustion considerably increases the kinetic energy of particles. The particles achieve supersonic velocities, the highest among thermal spray processes (Table 1).

The results are the most dense thermal spray coatings available where the coupling of plasticized particles can build up coatings with density approaching that of a bulk material. Also the uniformity of HVOF sprayed coatings is superior to the coatings prepared by other methods. Disadvantages of HVOF include low deposition rates, increased in-flight oxidation rates of the particles and limitations on applicable materials due to temperature constraints.

Fig. 2-9: Schematic of the HVOF technique [49]

Potential applications of HVOF overlap with plasma and detonation gun deposition: e.g. WC-Co coatings for increased fretting wear resistance of turbine components, wear resistant Co alloys coatings on fluid control valve seating areas, Ni-Cr coatings for increasing high temperature oxidation and corrosion resistance or hydroxyapatite coatings for bio-applications.

2.1.2.5 Plasma Spray

Plasma spray (Fig. 2-10) is generally regarded as the most versatile of all the thermal spray processes [50,51,53-55,62,63]. Thermal plasmas are generated in inductively coupled discharges (inductively coupled plasma, radio frequency plasma) or in direct electric arcs (direct current plasma) that are stabilized by flow of gases or water vortex. As a method employed in this study, *atmospheric DC plasma spray* (APS) will be solely discussed in the following text.

During APS process operation, gases or gas mixtures such as argon, helium, nitrogen and hydrogen are passed through a torch. An electric arc between coaxially aligned central cathode and water cooled anode gives the gas molecules enough energy to dissociate and ionize by

atomic collisions during their passing through an anode orifice. Beyond the nozzle, the atomic components recombine, giving off a tremendous amount of heat. Powder is injected externally or internally into the jet, melted and accelerated towards the substrate. The heat content, temperature and the velocity of the plasma jet are controlled by the torch geometry, the arc current, the gases flow rate and/or mixture ratio.

Fig. 2-10: Schematic of the DC plasma spray technique [49]

As seen from Table 1, the plasma core temperatures reach values up to 16000 K, well above the melting point of any solid material. Plasma spray can therefore be used for spraying of materials unsuitable for other techniques.

The relatively low velocity of particles as compared to e.g. HVOF or detonation gun deposition results in coatings with higher porosity level and lower bond strengths.

Plasma spray remains the most commonly used method off all the thermal spray processes. Its versatility provides a broad spectrum of usage, e.g. Zr-based thermal barrier coatings (TBC) on turbine combustion chambers, wear resistant Al_2O_3 and Cr_2O_3 coatings on printing rolls designed for subsequent laser and diamond engraving and etching, Mo-alloys coatings on diesel engine pistons or, one of the most recent plasma spray applications, biomaterial coatings of hard tissue prostheses.

Several *specific features* are to be taken into consideration for atmospheric DC plasma spray process. Final in-flight properties of the material particles introduced into the plasma jet

are strongly correlated to the plasma jet properties [64,65] and also to the geometrical setup of material feeding.

Properties of the plasma jet are directly influenced by the *plasma system parameters* (PSP) settings and the choice of *employed gases*. For its importance as one of the focal points of this study, the influence of PSP will be discussed in detail in chapter 3.1.1.1.

The choice of employed gases and a presence/absence of *secondary and/or tertiary gas* (auxiliary gases) has a major effect on the generated jet properties. Argon and nitrogen are generally used as primary gases as their high atomic masses ($m_a(\text{Ar}) = 39.948$, $m_a(\text{N}_2) = 20.180$) contribute to the arc stabilization and provide flow necessary to propel the introduced material [62]. Inert argon is preferable to prevent reacting with introduced material or substrate in the process and its low ionization potential (compared to nitrogen) allows easier arc ignition. Helium and hydrogen are usually used as auxiliary gases to increase the plasma enthalpy (typically, $1 - 30 \text{ MJkg}^{-1}$), conductivity and to further increase the plasma velocity. Relative properties of various conventionally employed primary gases or gas mixtures are summarized in Table 2.

Table 2: Relative properties of gases and gaseous mixtures used in plasma spray [66]

Gas	Ar	Ar + He	Ar + H ₂	N ₂	Air
Arc voltage	lowest	medium	medium	high	high
Plasma jet enthalpy	lowest	high	high	medium	medium
Plasma jet temperature	high	highest	medium	lowest	medium
Plasma jet velocity	medium	high	high	low	medium
Thermal efficiency	lowest	medium	medium	high	medium
Electrode wear	low	medium	medium	medium	highest
Cost	high	highest	high	low	lowest
Noise	lowest	low	medium	high	high

Another aspect of the choice of used gases are the differences in *temperature and velocity distribution fields*. The differences originate from the different thermal and momentum qualities of used gases and typically have steep spatial gradients, particularly in the radial direction. Typical levels of temperature and velocity at different distances in Ar + H₂ generated plasma jet are demonstrated in Fig. 2-11 and Fig. 2-12, respectively. Typically, the *gradients* reach values of up to 10^7 Km^{-1} in temperature and $5 \cdot 10^5 \text{ ms}^{-2}$ in velocity.

Fig. 2-11: Typical temperature isocontours in Ar+H₂ generated plasma

Fig. 2-12: Typical axial velocity isocontours in Ar+H₂ generated plasma

Due to the spatial distributions of temperature and velocity of generated plasma, particle trajectory within the jet is an essential factor in terms of material heating, melting and/or

vaporizing and kinetic energy increase. Vital in-flight particle properties such as temperature and velocity are therefore influenced by geometrical setup of the system, particularly by the process of material feeding into the jet.

In the literature, *three factors* are generally indicated as *critical for the particle trajectory* shape determination: the amount of *carrier gas* used to carry the powder particles from the container into the jet, the *position* and orientation of the *powder injector* with respect to the plasma torch nozzle and the various *sizes of particles* within a feedstock.

Known as *carrier gas effect* [26,67], the former factor was studied thoroughly in recent years. It was found that there are three significantly different ranges of carrier gas flow. If the carrier gas flow is too low, the particles within it do not have enough momentum to penetrate into the core of the fast flowing plasma jet and either are deflected into the surrounding area or travel on the much colder periphery of the jet, resulting in improper melting and coating properties deterioration. The deflection of particles typically occurs for carrier gas flow corresponding to 10% of the plasma gases flow rate [39]. In addition, too low carrier gas flow generally causes little or no particle delivery into the powder injector. In case the carrier gas flow rate is too high, particles intersect the plasma jet hot core and travel on the reverse side of the jet or are not propelled towards the substrate at all, again resulting in poor coating qualities. Optimally, adequate carrier gas flow rate is used, guaranteeing even heating of the particles and kinetic energy transfers (Fig. 2-13). The carrier gas effect is more evident for fine particles and/or low density materials.

The second factor represents the mutual geometrical aspect of the powder feeder and the plasma torch nozzle. Two different configurations are commonly used: *external powder feeding* (Fig. 2-13) where the powder is introduced into the jet outside of the plasma torch and *internal*, where the powder feeding hose leads the powder into the orifice in the anode. Due to steep gradients in temperature and velocity fields in the vicinity of the anode orifice, the seemingly negligible difference in injector position frequently results in significant differences in particles in-flight properties [26].

In addition, influences of both configurations can be altered by modifications in the direction of powder feeding. Susceptible to the carrier gas effect, the commonly used *radial*

feeding is sometimes replaced by angle feeding or *axial feeding*. In angle feeding, the principal axis of the powder feeder forms an angle with the plasma torch centerline, supporting the desirable suppression of the carrier gas effect by introducing axial velocity vector component. Axial feeding eliminates the carrier gas effect entirely.

Fig. 2-13: Carrier gas effect

The latter referred factor influencing particles trajectories within the jet represents the various *sizes of particles* within a feedstock. The considerations on the previous two factors were referring to average particle trajectories of ideally single-sized powder feedstock. However, the real feedstock comprises of a range of particles of *different radii* and, therefore, different volumes and weights, resulting in *different momentums* and penetration into the plasma jet in dissimilar ways. The phenomenon of powder particles size influence was studied extensively elsewhere and is not part of this study. To eliminate the effect in the presented experiments, all powders used were thoroughly sieved into narrow particle size ranges (4.2).

Powder feeding is sometimes reported as another factor influencing the particle in-flight properties. With increasing powder feed rate, the enthalpy and momentum of thermal plasma has to be distributed among a higher number of particles which could result in decrease in measured temperatures and velocities.

2.1.2.6 Cold Spray

The innovative low-temperature *cold spray* process [68-75] is regarded as one of the thermal spray techniques. In cold spray (cold gas-dynamic spray, kinetic spray, Fig. 2-14), a

compressed gas such as helium, nitrogen or air is introduced to an electric furnace (pressure gas) and a powder feeder (feeder gas). The pressure gas is moderately heated and exits the spray gun via a conical convergent-divergent Laval nozzle [76-78] accelerated to supersonic velocities. Feedstock powder is injected axially into the gas flow at the gun nozzle intake and accelerated to velocities of $300 - 1200 \text{ ms}^{-1}$ [68,69]. Contrary to its high-temperature counterparts, cold sprayed coating is not built up by means of melting and solidifying of impinging particles. Solid-state plastic deformation and fusion of particles occurs instead, producing dense coatings without the feedstock material being significantly heated [68-71].

Fig. 2-14: Schematic of the cold spray technique

The latest of all the processes in thermal spray family, cold spray is the next progressive step in the development of high kinetic energy coating processes. It follows the trend of increasing particle spray velocity and reducing particle temperature. Due to its ambient-temperature character (Fig. 2-5), cold spraying eliminates the detrimental effects of high temperature experienced with other thermal spray techniques. Phase and composition changes of the original feedstock are negligible and residual stresses induced by high temperatures are lower, allowing production of thicker coatings. Substantial reduction of material oxidation in cold-sprayed coatings results in dramatic increase of thermal and electrical conductivities. The absence of oxides improves the intrinsic bonding strength, resulting in the highest adhesion strengths among thermal spray processes. Coating hardness is also improved. Furthermore, cold spray allows spraying materials with low decomposition temperatures, unsuitable for high-temperature treatment, e.g. polymers. Other advantages of cold spray technique include

reduced material loss by vaporization, low gas entrapment and insignificant grain growth and recrystallization. High spray rates (up to 10 kg hr^{-1}) and deposition efficiency (up to 70%) allow fast coating build-ups of about $250 \mu\text{m}$ per pass. In cold spray, due to the internal axial nature of powder feeding, carrier gas effect is fully suppressed. High production cost due to increased gas consumption is the limiting factor of the process. A choice of coating materials is limited to ductile materials as hard and brittle materials like ceramics can not be sprayed in a pure form. Substrate materials are also limited to those that can withstand the aggressive action of the sprayed particles (soft or friable substrates will erode rather than being coated). Enhancement of the lifetime and dimensional stability of system key components (nozzle) which are subject to the abrasive nature of process is also an unsolved issue.

Typical applications of cold spray technology include coatings with increased thermal conductivity, wear and fatigue resistant coatings on biomedical implants, deposition of electrical conductors in electronics industry, corrosion protection coatings with enhanced performance due to low oxide content and deposition onto glass or aluminum and other comparatively low-temperature melting substrate materials to locally increase hardness or wear resistance.

As well as plasma spray, cold spray has some *unique features* as compared to other thermal deposition techniques. Bonding of particles occurs solely when the impact velocities of particles exceed a critical value [75]. This *critical velocity* depends on the type of spray material, the powder quality, particle size and the particle impact temperature. Particles cold sprayed below the threshold value merely act as abrasives, a process similar to grit-blasting.

The *convergent-divergent Laval nozzle* is a tube that is constricted in the middle, creating an hour-glass shape. Its operation relies on the different properties of gases flowing at subsonic and supersonic speeds. The speed of a subsonic flow of gas increases if the pipe carrying it narrows because the mass flow rate is constant. At subsonic flow (Mach number < 1.0) the gas is compressible; sound can propagate through it. Near the middle part of the nozzle, where the cross sectional area is minimal, the gas velocity locally becomes transonic (Mach number $= 1.0$), a condition called choked flow. As the nozzle cross sectional area increases the gas continues to expand and the gas flow increases to supersonic velocities (Mach number $>$

1.0); a sound wave will not propagate backwards through the gas. The *exit velocity of the gas flow* at the exit of Laval nozzle can be calculated under some simplifying assumptions:

- the gas is assumed to be an ideal gas
- the gas flow is isentropic (constant entropy), the flow is reversible (frictionless and no dissipative losses) and adiabatic (i.e., there is no heat gained or lost)
- the gas flow is constant and steady during the period of the process
- the gas flow is along a straight line from gas inlet to the gas exhaust exit, i.e. along the nozzle axis of symmetry
- the gas flow is compressible since the flow is at high velocities.

Assuming these conditions, the exhaust velocity of the gas at the nozzle exit is given as:

$$v = \sqrt{\frac{TR}{m_a(\text{gas})} \cdot \frac{2k}{k-1} \cdot \left[1 - \left(\frac{P_e}{P} \right)^{\frac{k-1}{k}} \right]} \quad \text{Eq. 1}$$

where $k = \frac{c_p}{c_v}$ is the isentropic expansion factor, c_p and c_v are the specific heats of the gas

at constant pressure or volume, respectively, T is the absolute temperature of inlet gas, R is the ideal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$), $m_a(\text{gas})$ is the molecular weight of used pressure gas and P_e and P are the absolute pressures of exhaust gas at nozzle exit and inlet gas, respectively.

Bonding in cold spray is associated with adiabatic shear instabilities caused by *high strain deformation rate* during impingement. Pre-heating of materials by hot gases (up to 700 K) is used to aid in particle deformation as well as usage of high gas pressures (up to 3.5 MPa) and flow rates (up to $90 \text{ m}^3\text{hr}^{-1}$).

2.1.3 Inherent Coating Characteristics

As the thermal spray process takes place, a coating of deposited material is created on a substrate. Its thickness is influenced by the velocity of movement of a robotic arm, material deposition rates and number of successive torch passes. Each pass forms a layer of material adjacent either to a substrate (first layer) or previously deposited layers. The coating structure is therefore exposed to *thermal shocks* induced by the successive passes of the torch. Due to the heat fluxes of the plasma and impacting particles, the deposited material undergoes *phase and structural changes, oxidation and/or chemical decompositions and selective component evaporations*.

Various phases possess different, occasionally contradictory physical, chemical and biological properties. Adverse phase transformation stresses could arise due to phase changes. Chemical alterations and selective evaporation change the precisely balanced composition of initial feedstock, particularly in case of blended powder mixtures or graded coatings. Due to different growth processes, additional stresses can be induced. A presence of hard oxide agglomerates can alter some basic physical properties of the coatings. The properties of the final coatings therefore usually vary significantly from those of the feedstock material, often resulting in deterioration in targeted performance. Chemical and phase composition analysis of coating is therefore of utmost importance in evaluation of final coating properties and is an important part of the experimental work carried out within this study (3.2.2.3).

During the deposition process, much of the heat from plasma jet, heat contained within the impinging particles and the solidification heat is removed by conduction through the substrate. In most cases, such conduction is not sufficient, giving rise to the development of *thermal stresses* [6,19,20,79-85]. The stresses can be divided into two classes [86,87]: primary (*quenching*, deposition) stresses and secondary (*differential thermal contraction*) stresses.

The former stresses develop immediately after impingement of a particle as a result of fast thermal contraction of solidifying splats. As the molten particles solidify they contract, but are constrained by each other and the substrate, generating stresses of a *tensile nature* in the individual splats. These stresses can only be alleviated by the introduction of micro-cracks in the material or debonding from the substrate.

The latter stresses arise from the mismatch in thermal contractions of a substrate and a coating upon cooling to ambient temperature. These stresses are *usually dominant* among all the stresses and are a function of the coating thickness (generally, the thicker the coating, the higher the absolute value of secondary stresses) [88]. Whether the secondary stresses in a coating are *tensile* or *compressive* depends upon the relative values of thermal expansion coefficient of substrate (α_s) and coating (α_c). If, as the temperature decreases, the coating contracts to a greater extent than the substrate (i.e. $\alpha_c > \alpha_s$), a tensile stress is generated in the coating. However, if the coating contracts by a smaller amount than the substrate (i.e. $\alpha_c < \alpha_s$), the resulting secondary stresses will be compressive. If the coefficients are equal, no secondary

stresses will develop. Frequently, pre-heating of a substrate is used to decrease the magnitude of secondary stresses. This method, however, can not be used universally as substrate heating could have detrimental effect on the content of oxides between the first adjacent layer and a substrate, resulting in poorer coating bonding.

Secondary stresses superimpose on the quenching stresses and the nature of the overall residue stresses depends on a character and magnitude of both components. If the secondary stresses are tensile or non-existent, the resulting stresses will be tensile. In case the secondary stresses in a coating are compressive, mutual magnitude of primary and secondary stresses (a function of coating thickness) determines the overall stresses in a deposit (Fig. 2-15).

Fig. 2-15: Typical stress distribution in coated specimen

Total tensile stresses in a coating lead to *bond strength reduction, adhesion loss and cracking of the coating*, promoting local coating debonding and, in case of relatively thick coatings, could lead to delamination.

Delamination, i.e. tearing off adjacent layers, is a coating material degradation process in which the cracks propagate in a direction parallel to the substrate - coating boundary [86]. Delamination is initiated at the component edges or at the points of high stress concentrations such as inclusion or extraneous oxide particles. A local delamination between a substrate and a

first layer of a coating could result into a detachment of the entire coating and immediate system breakdown.

In case a thermal sprayed component is subject to external tensile loads, the most frequent failure mode is a *fracture* of the coating. The fracture occurs in a direction perpendicular to the substrate - coating boundary as a result of coalescence of intra-splat micro-cracks. The propagation of the crack is driven by the deformation of the substrate. A selection of substrate and coating materials leading to a development of compressive stresses reduces this effect.

Post deposition treatment methods are employed to relieve internal stress in coated bodies. Among others, laser ablation of a coating surface or a coated component annealing and/or normalizing are the most commonly used. Description of stress relieving methods is beyond the scope of this work and will not be discussed further.

Existence of the thermal stresses needs not to be inevitably detrimental. The superposition of internal stresses of coated specimens and external load could lead to an overall decrease in the total stress values, increasing the values of *fatigue lives* up to ten times as compared to that of non-coated bodies [86,87]. Experimental work pertaining to this phenomenon forms one part of this study and will be discussed in detail in section 3.2.3.1.

Splat by splat, the coatings are built up, having its inimitable, messy structure. Consisting of solidified splats, unmolten or semi-molten particles, various impurities such as inclusions and/or oxidized particles, micro-scale cracks, gas filled voids and inherent porosity (Fig. 2-4), the *coatings are largely heterogeneous, anisotropic and consisting of both amorphous and recrystallized phases in various polymorphic forms.*

Microstructure of deposited layers significantly influences the overall coating properties. A presence of impurities, unmolten particles, various inclusions and material oxides, as well as amorphous content, micro-cracks density and polymorphic composition alter the properties in diverse ways and will be studied in the following text in detail (3.2.2.2).

Distribution and total *porosity content* are of vital importance for the intended performance of coated components. Porosity causes changes in intrinsic material properties (coating density, Young's modulus of elasticity - approximately 3x to 10x lower than that of a bulk material for metallic or ceramic coating, respectively) and allows the coating to follow deformations of

substrate up to several percent effortlessly [88,89]. Higher porosity levels are desirable e.g. for thermal protection applications, where the voids contained within the coatings decelerate heat propagation, resulting in excellent thermal insulation properties. Defined porosity levels and specific average pore sizes are e.g. crucial in biomedical applications, supporting living tissues in-growth into the coated implant. Due to its importance, several experimental methods were used in this study to evaluate the porosity content and average pore sizes within deposited coatings (3.2.2.4).

Anisotropy of some coating characteristics occurs as a consequence of disordered structure [88-90]. A typical example is the distinctive direction dependence in values of coatings Young's moduli and Poisson's ratios. Coatings exhibit different behavior when subjected to external tension and compression [88], a consequence of opening and partial closing of internal spherical pores. Furthermore, non-linear behavior is reported under compression, which could be caused by full closing of small voids and micro-cracks, approaching the properties of a bulk material.

Adhesion of thermally sprayed coatings is of utmost importance with respect to the lifetime performance and proper functionality. Apart from the material choice, adhesion is influenced by several other factors: coating thickness (generally, the thicker the coating, the lower is the adhesion strength), residual stresses character and magnitude, material in-flight oxidation, substrate surface preparation (greases, oils, roughness) and the process parameters. For its importance, adhesion strength testing of sprayed specimens was carried out (3.2.2.6). In principle, cohesion strength of sprayed coatings imitates adhesion strength in terms of diverse influences arising from various parameters.

Different problems than those encountered in plasma spray are usually encountered for coatings produced by *cold spray technique*.

The *thermal load* on the substrate and preceding layers from consecutive torch passes is *minimal* as compared to high-temperature spray processes. Primary and secondary thermal stresses are negligible and therefore the stresses originating from the substrate deformation upon particles impingement (peening stresses) and/or *plastic deformation stresses* within

individual splats become dominant. Due to its relatively small magnitude, the resulting coatings are subject to relatively small residual stresses.

Subsequently, coating delamination and decohesion is restrained and overall coating *adhesion* is significantly *improved*, reaching up to 300 MPa (Table 1), higher than the coatings produced by other thermal spray techniques.

Due to *decrease in porosity* content, coating cracking under application of tensile external stresses is more accentuated and cold sprayed coatings are susceptible to this failure mode.

Cold spray technology produces coatings with *little or no phase and structure changes* as compared to the original feedstock, post-spray heat treatments to restore initial phase composition are therefore unnecessary. Chemical decomposition or selective component evaporation are virtually non-existent as the working temperatures in cold spray remain well below melting temperatures of most sprayed materials. In-flight *oxidation* of sprayed material, a process intensified at elevated temperatures, is *suppressed*. Increase in amorphous content of original feedstock, characteristic for all high-temperature processes, is negligible in case of cold spray.

All cold sprayed particles are solid and merge in this unmolten state. This fact entails a problem not encountered in other thermal spray coatings: a bonding of the first layer to a substrate is diametrically different from a bonding between individual layers. For certain materials (e.g. ceramics), *coating build-up*, i.e. growth in thickness by successive layers deposition could be limited.

2.2 Biomaterials

Factors like diseases, traumas, acute injuries, hereditary and genetic disorders, lifelong collection of toxicants and, most of all, aging, reduce the ability of a human body to replace defective or necrotic cells and repair damaged tissues. The genesis of *medical sciences*, the means of suppressing the impact of these negative factors, can be traced back to the beginnings of ancient civilizations. With the evolution of these sciences, aiding healing, correcting deformities or restoration of lost functions of various parts of human body has become progressively successful.

A special part of medical sciences are the endeavors to partially or fully *repair or replace defective tissues or body organs*. The pioneer attempts in this area often resulted in unwanted consequences like infections, embolism or tissue inflammation or necrosis which generally caused additional difficulties like worsening of patient's hardship, contiguous systems malfunctions, or, in the worst case, death.

The intensifying public demands for development of this part of medical sciences evoked a rapid progress. It was not until 1860s when the advent of aseptic surgical techniques allowed an unprecedented boom in this area. After overcoming the primary problems with surgical methodology, the focus of research turned to a second milestone: *the materials*.

Initially, the empirical methodology of surgery allowed only usage of limited range of materials, affordable and easy to acquire, process and manufacture. Wood, a natural high strength-to-weight ratio composite, was used for limb prostheses and artificial teeth. Gold, a malleable and inert metal, was used in dentistry. Iron and brass were used to rejoin fractured bones as well as original bone structures from other mammals (e.g. ivory). Glass was used as an eye replacement due to its cosmetic appearance. Eventual success in application of such *traditional materials* was more accidental than by design and these materials have become *insufficient* and the need to find suitable materials capable of being applicable into human body became critical around 1960s [62].

It was clear that the materials stand for the major hindrance in the area of human surgical operations. The approach of usage of traditional materials in surgery was reassessed and novel types of materials were introduced. Surpassing the benefits and performance of the traditional materials, this new group of materials remains the source of intensive research until today. Generally known as *biomaterials*, they provide the solution to many problems encountered in this area of medical sciences.

2.2.1 General Overview

2.2.1.1 Biomaterials Taxonomy

The variety of the present-day biomaterials and the broad spectrum of their usage led to a disunity in a definition of the term. The *definition* evolved and tracing its changes could help to get basic understanding on the marginal steps in biomaterials concept:

Table 3: Historical evolution of definition of biomaterials [62,91-94]

Year	Definition
1974	A systemically and pharmacologically inert substance designed for implantation within or in corporation with living systems
1980	Materials of synthetic as well as natural origin in contact with tissue, blood, and biological fluids, and intended for use for prosthetic, diagnostic, therapeutic, and storage applications without adversely affecting the living organism and its components
1982	A biomaterial replaces a part or a function of the body in a safe, reliable, economic and physiologically acceptable manner
1986	A non-viable material used in a medical device, intended to interact with biological systems
1987	Any substance (other than a drug), synthetic or natural, that can be used as a system or part of a system that treats, augments, or replaces any tissue, organ, or function of the body
1995	A solid materials that occur in and are made by living organisms, such as chitin, fibrin or bone
1999	A synthetic or natural material used to replace part of a living system or to function in intimate contact with living tissue
1999	A synthetic, natural or modified natural material intended to be in contact and interact with the biological system

The definition which is worldwide acknowledged is a refined version of the 1986 definition (the reference to non-viable materials was also removed) and dates to 1991: *A biomaterial is a material intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body* [95]. Artificial materials that simply are in contact with the skin, such as hearing aids and wearable artificial limbs are not biomaterials, since the skin acts as a barrier.

A *biological material* is defined as a material produced by a biological system. When biomaterials come into contact with original biological materials, various *responses of the host tissues* could arise, ranging from completely hostile reaction (e.g. biomaterial refusal, self-defensive mechanisms activation, tissue damage), neutral reaction (e.g. tissue inert) to positive tissue response (e.g. biomaterial acceptance, mutual bonds formation, implant incorporation). The extent and nature of the host tissues response depends on the biological properties of the biomaterial and is generally known as its *biocompatibility*.

High biocompatibility (the ability of a material to perform with an appropriate host response in a specific application) is the first and most important condition imposed on present-

day materials. Materials not meeting this criterion (materials with undesirable effects, secondary side effects) are no longer acceptable for medical and/or surgical purposes. Required levels of biocompatibility depend, among other factors, on the contact time between biomaterial and biological tissue, from few seconds ranges where the requirements need not to be strict (e.g. syringe needle, tongue depressor) to periods of several decades where ultimate biocompatibility is an imperative (e.g. bone screws, total hip replacement).

The biocompatibility indicates the response of the host tissues when in contact with biomaterial. Furthermore, there is also a level of *interaction* from the biomaterial. Basically, three different designs are used [62,96]:

Bioinert materials are non-toxic and remain chemically stable even at long-term application times (years). Usually, a thin fibrous tissue surrounding the bioinert implant is formed as a tissue reaction. There are currently attempts to replace these first generation materials with pro-active functioning materials. Stems of orthopedic implants or dental replacements are made of bioinert materials.

Bioresorbable (biodegradable) materials are gradually resorbed by the body. Sometimes the decay of a biomaterial is followed by a replacement with new tissues. The process usually ends when the biomaterial fully vanishes or is fully replaced by biological tissues. Controlled drug-delivery systems or vascular grafts and nerve guidance channels are made of bioresorbable materials.

Bioactive materials actively elicit a specific biological response at the interface, usually resulting in a formation of a bond between the biomaterial and surrounding tissues. Bioactive materials are intermediate between bioresorbable and bioinert as they can retain both designs. Surface coatings of hard tissue implants or skin tissue implants are made of bioactive materials.

Bioactive and bioresorbable materials are referred to as second generation. Third generation materials are bioactive materials with external activation of surrounding tissue cells and genes. The activation is based on stimulation of specific cellular responses at a molecular level.

2.2.1.2 Biomaterials applications

The intensive research and development provided a wide variety of biocompatible materials suitable for surgery. An option to choose from a number of suitable materials

broadened its utilization scope. At present, the range of *biomaterials applications* includes almost every system of a human body (Fig. 2-16).

Fig. 2-16: Usage of biomaterials in various body systems

Basically, current applications of biomaterials in a human body could be divided into *three major domains* according to the intended activity type: assistance, repair and replacement applications.

Assistance applications, i.e. aiding the biological system in performing its function, include dental repairs, caps, cavity fillers; cardiac pacemakers, cardiac assistive devices; contact lenses; scoliosis spine device; lung oxygenator machine; kidney dialysis machine; cosmetic surgery materials, augmentation mammoplasty, chin augmentation.

Common examples of *repair applications* (aiding the biological system as it physiologically restores its function) are fracture fixation devices; bone cement, bone plates; sutures; catheters, drains, shunts; burn dressings; artificial skin.

Removing the original system and substituting it with artificial biomaterials (*replacement applications*) is performed in case of artificial heart, heart valve [97]; heart-lung machine; blood vessel replacement; cochlear replacement; eye lens replacement, glass eye; dentures, bridges; ligaments and tendons; intervertebral discs; artificial joints: hips, knees, shoulders, ankles, wrists, elbows.

The area of *artificial joint replacements* is one of the most demanding applications in terms of biomaterials choice. A combination of requirements for a successful integration, chemical and physical stability, long service life and, above all, perfect and painless functionality accentuates the need for materials with the highest biocompatibility. As a single biomaterial can not suffice to the demands, a suitable combination of biomaterials is usually used within a single prosthesis.

In case of a hip prosthesis for *total hip arthroplasty* [98-100] (Fig. 2-17), minimization of wear and friction between the acetabulum (hip socket) and femoral head is essential while preserving the joint versatility. Formation and release of wear debris could result into breaking of implant head due to additional stresses concentration, subsequent vascular problems or loosening of the implant due to wear debris presence. Corrosion and ion release should be imperceptible during the entire service life of the prosthesis as these may have undesirable effects.

Fig. 2-17: Advanced technology hip prosthesis [101]

It is necessary to guarantee satisfactory mechanical resistance to the high external flexural and torsion stresses. Basically, this is achieved by design of the prosthesis stem. Polymers do not possess adequate mechanical properties while ceramics stems are unsuitable due to its inherent brittleness, *metal stems* are therefore used instead [102,103]. However, the metal

stems of the prostheses generally have higher stiffness than that of a natural bone. The consequence of this stiffness mismatch is that the biomaterial implant carries most of the mechanical load and shields the original bone from participating. Unloaded living bones tend to retard and undergo biological changes leading to weakening of the bone and deterioration of the implant-bone interface [104]. Therefore, *low-stiffness* (low Young's modulus) metal stems are *desirable* [105,106].

Stem and acetabulum *fixation into the bone* is of utmost importance. Apart from mechanical interlocking mechanism (inclusive of the component's surface roughness on a microscale), two different approaches are used. Older method consists in using *bone cement* (Fig. 2-18) [107-111] for fixation of the parts to the skeleton. However, the cement acts merely as filler, its lifetime is relatively limited and it may cause necrosis of surrounding tissue due to high temperatures during its curing process [109,112].

Fig. 2-18: Cemented and cementless hip prosthesis [111]

Another method consists in *covering the stem and/or acetabulum with biomaterials* that provide a scaffold matrix for original bone in-growth (*osteoconductor*) or actively stimulate formation of a new bone (*osteoinductor*). To support the bone in-growth, a certain range of porosity in the scaffold matrix is desirable (usually 5 - 20%) [113-115]. High porosity results in mechanically weaker coatings prone to cracking. The views on ideal pore size vary considerably in the literature. In general, small pore sizes restrict bone cells (osteoblasts) from expanding into the coating. Adequate adhesion of the osteoconductive/osteoinductive coatings

is vital as eventual coating delamination and subsequent stem exposure could lead to an infective refusal of prosthesis.

Probability of failure due to any of the degrading factors for the total hip joint implant is depicted in Fig. 2-19. The prosthesis in the figure malfunctioned due to a rupture of its ceramic head, a consequence of stress concentration due to a presence of wear debris between the head and acetabulum.

Fig. 2-19: Degrading factors of total hip joint implant

A total hip joint replacement represents relatively non-complex case. Nevertheless, there are many latent problems and there is still a risk of imminent failure. An essential factor in determining the quality and performance of the prosthesis is a choice of used biomaterials.

2.2.2 Materials used

Suitable biomaterials could be found among any type of chemical compounds. Usage of biomaterials is given by the specific needs of a particular application with respect to their strong points and considering their weaknesses. Taking advantage of particular materials properties for *targeted applications* is essential.

Individual biomaterials properties are largely given by the common properties of the group of materials where the material appertains. Metals or metal alloys, ceramics and glasses, polymers and various composite materials are the main groups of materials commonly used as biomaterials. Some basic characteristics of different types of materials are given in Table 4.

Table 4: Relative properties of various material types

Materials	Bonding	Microstructure	Advantages	Disadvantages
Metals and alloys	metallic	crystal grains	strong stiff ductile conductive	low fatigue resistance high weight
Polymers	covalent	chain molecules	low cost light weight resist corrosion	low strength low stiffness creep wear
Composites	various	matrix fiber particles granules	strong stiff light weight	high cost delamination
Ceramics and glasses	ionic, covalent	crystal grains amorphous	strong stiff hard resist temperature resist corrosion	brittleness prone to fracture

A selection of the *best suitable biomaterials* for a specific application is influenced by design requirements (function, objectives, constraints), anticipated loading (expected service life, mechanical loading, environmental impact) and also its availability and cost [116,117].

For the production of a successful implant, a number of material properties has to be considered: *mechanical properties* (e.g. elasticity modulus, strength, ductility, hardness, toughness, Poisson's ratio, fatigue limit, density and porosity), *chemical properties* (e.g. toxicity, reactivity, corrosion resistance, ion release), *thermal properties* (e.g. thermal conductivity, coefficient of thermal expansion, phase changes), various *electrical and magnetic properties* as well as *optical properties*.

2.2.2.1 Conventional materials

Metals and metallic alloys have a broad range of applications, e.g. as orthopedic or dental implants. Stainless steels (e.g. 316L/SS) are used for production of temporary devices like fracture plates and screws, stents or surgical instruments. Having excellent corrosion resistance, cobalt alloys (Co-Cr-Mo, Co-Ni-Cr-Mo) are frequently employed to produce bone and joints replacements, dental implants or restorations or heart valves. Ni-Ti alloys are used for bone plates, stents or orthodontic wires. For dental restorations, gold or Hg-Ag-Sn amalgams are used. Pt and Pt-Ir alloy are used to manufacture medical electrodes and silver-based alloys are used for production of antibacterial agents. Titanium and titanium-based alloys (pure Ti, Ti-Al-Nb, Ti-13Nb-13Zr, Ti-Mo-Zr-Fe) are a popular use for production of bone and joint replacements, fracture fixations, dental implant or pacemaker encapsulations.

In case of bone and joint replacements, *Ti-6Al-4V* alloy gained a special importance recently [1,2,18,105,118-126]. The alloy satisfies the need to find a chemically stable, biocompatible substrate with relatively low elastic modulus and excellent corrosion resistance able to carry the mechanical load (Table 5).

Table 5: Average densities and elastic moduli of bones and metallic alloys for bone and joint replacements [105]

Material	Average density [gcm ⁻³]	Elastic modulus [GPa]	Elastic modulus/average density [GPa/gcm ⁻³]
316L steel	8.0	200	25.0
Co-Cr alloys	8.5	230	27.0
Pure Ti	4.51	110	24.4
Ti-6Al-4V	4.42	114	25.8
Cortical bone	1.8 - 2.2	17 - 27	9.4 - 12.3
Trabecular bone	1.5 - 1.9	1 - 11	0.7 - 5.8

Initially developed for aerospace applications (ASTM F136, Grade 5), Ti-6Al-4V implants do not induce allergic reactions, as sometimes observed with some stainless steels. Its low density enables production of light-weight prostheses. Some basic properties of Ti-6Al-4V alloy are given in Table 6.

Table 6: Basic properties of Ti-6Al-4V alloy [1,121,122]

Property	Typical value
Density	4.42 gcm ⁻³
Melting point	1649 K
Specific heat	0.56 Jkg ⁻¹ K ⁻¹
Thermal conductivity	7.2 Wm ⁻¹ K ⁻¹
Coefficient of thermal expansion (0 - 373 K)	8.6 x10 ⁻⁶ K ⁻¹
Coefficient of thermal expansion (373 - 573 K)	9.2 x10 ⁻⁶ K ⁻¹
Tensile strength	1.00 GPa
Elastic modulus	114 GPa
Poisson's ratio	0.31
Hardness (Rockwell)	36

The exact chemical composition of the alloy is set by the ASTM standards (Table 7).

Table 7: Chemical composition of Ti-6Al-4V alloy

Element	Ti	Al	V	Fe	O ₂	H ₂	C	N ₂
Content [weight %]	balance	5.5 - 6.76	3.5 - 4.5	< 0.25	< 0.2	< 0.12	< 0.08	< 0.05

A variety of *polymers* are used as biomaterials [127-129]. Their applications range from facial prostheses to tracheal tubes, kidney and liver parts, heart components, dentures and hip and knee joints. Polymer materials are used as medical adhesives and sealants and for coatings that serve a variety of functions. Poly(tetra fluoroethylene) (PTFE), formerly used for soft-tissue augmentation and some vascular prostheses, was replaced by polyethylene and ultra-high molecular weight polyethylene (UHMWPE) for joint replacements. Sutures are manufactured from polypropylene, various polyamides and poly(ethylene terephthalate) (PET). Polyesters are used for vascular prostheses as well as for drug-delivery systems. Parts in contact with blood are usually covered with a thin layer of polyurethanes. Poly(vinyl chloride) (PVC) is used for production of various tubings. Poly(methyl methacrylate) (PMMA) is the most common example of cement for bone and joint prostheses (2.2.1.2). It is also used for dental restorations and production of intraocular lenses. Silicones are popular polymers for use in soft-tissue replacements or ophthalmology and for production of catheters and tubings. Various hydrogels are used in ophthalmology and for production of drug-delivery systems. Cellulose is used for production of dialysis membranes. Reprocessed collagen is used to produce wound dressings.

The most successful *composite biomaterials* are used in the field of dentistry as restorative materials or dental cements (PMMA-glass fillers) [130]. Although e.g. carbon-carbon and carbon-reinforced polymer composites are of great interest for bone repair and joint replacement because of their low elastic moduli levels, these materials have not displayed a combination of mechanical and biological properties appropriate to their applications. Composite materials are, however, used extensively for prosthetic limbs, where their combination of low weight and high strength make them ideal materials for such applications.

Traditionally, *ceramics* have seen wide scale use as restorative materials in dentistry. These include materials for crowns, cements, and dentures (various porcelains). Alumina (Al_2O_3) and zirconia (ZrO_2) ceramics are used in joint replacements (e.g. the femoral head and the inner part of acetabulum cup in a total hip arthroplasty) [131,132]. Carbons were tested for heart valves or dental implants and variant bioactive glasses were used for artificial eyes or bone replacements.

Due to their intrinsic properties and suitability for thermal deposition onto metallic implants, *calcium phosphates* gained privileged position among all ceramic materials. Composed of calcium ions (Ca^{2+}), orthophosphates (PO_4^{3-}), pyrophosphates ($\text{P}_2\text{O}_7^{4-}$), cyclic metaphosphates ($\text{P}_3\text{O}_9^{4-}$, $\text{P}_4\text{O}_{12}^{4-}$) and/or hydrogen or hydroxide ions (OH^-), calcium phosphates are a group of mineral materials naturally occurring in bones and bony structures. They *form 69% of human bone tissue* (Table 8), therefore they are the first choice materials for artificial biocompatible substitutions of bones in medical science [134-137].

Table 8: Typical human bone composition [133]

Component	Content [weight %]
Calcium phosphates	69
Collagen	20
Water	9
Proteins, polysaccharides, lipids	2

The members of calcium phosphates family are usually *differentiated by their Ca/P ratios* and denoted by their *abbreviations* for simplicity. Table 9 summarizes the chemical formulas, abbreviations and Ca/P ratio of some selected calcium phosphates. The basic relations between particular compounds could be seen from Fig. 2-20.

Table 9: Calcium phosphates [135]

Ca/P ratio	Formula	Name	Abbreviation
2.00	$\text{Ca}_4\text{O}(\text{PO}_4)_2$	Tetracalcium phosphate	TTCP
1.67	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	Hydroxyapatite	HA
1.67	$\text{Ca}_{10}(\text{PO}_4)_6\text{O}$	Oxyapatite	OHA
1.50	$\text{Ca}_3(\text{PO}_4)_2$	Tricalcium phosphate (α , β)	TCP
1.33	$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$	Octacalcium phosphate	OCP
1.00	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	Calcium phosphate dihydrate	DCPD
1.00	CaHPO_4	Calcium phosphate	DCP
1.00	$\text{Ca}_2\text{P}_2\text{O}_7$	Calcium pyrophosphate (α , β , γ)	CPP
1.00	$\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	Calcium pyrophosphate dihydrate	CPPD
0.70	$\text{Ca}_7(\text{P}_5\text{O}_{16})_2$	Heptacalcium phosphate	HCP
0.67	$\text{Ca}_4\text{H}_2\text{P}_6\text{O}_{20}$	Tetracalcium dihydrogen phosphate	TDHP
0.50	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	Monocalcium phosphate monohydrate	MCPM
0.50	$\text{Ca}(\text{PO}_3)_2$	Calcium metaphosphate (α , β , γ)	CMP
0.50	$\text{Ca}(\text{OH})_2$	Calcium hydroxide	-

Stoichiometric crystalline calcium phosphates are rarely found in human tissues. *Non-stoichiometric* substitutive compounds or certain *amorphous content* are usually *present*.

Fig. 2-20: Ternary system $\text{CaO} - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$

Mostly used in areas of contact between an implant and living tissue, the stability of calcium phosphates in human body is of key importance [133]. The prerequisite for *thermodynamic stability* comes from the fact that the absence of solid-state reactions allows thermodynamically unstable calcium phosphate compounds (e.g. TTCP) to retain their composition when cooled to ambient temperatures (Fig. 2-21). Stability and solubility in water environment (human body comprises 60 - 70% water) must also be considered.

Two different situations may arise when *metastable compounds* are exposed to an *aqueous solution* (e.g. in human body):

1. A *continuous dissolution* of the compound's surface

The dissolution continues until the surrounding solution is not saturated. This trend could lead to a subsequent failure of the implant by complete dissolution of the coating material, exposing the substrate.

Fig. 2-21: Phase diagram of CaO - P₂O₅ at a vapor pressure of 66.7 kPa [138]

2. Occurrence of the surface reactions leading to a *precipitation* of a second, *stable* phase

Precipitation of another, stable phase from an aqueous solution occurs when the solution is super-saturated with the particular mineral compound. Conversely, dissolution of a compound occurs when the surrounding aqueous solution is under-saturated. The degrees of super- and under-saturation are the driving forces in precipitation and dissolution reactions. The rates at which dissolution and precipitation occur are decisive for the final implant stability. Typical example is the formation of HA on the surface of TTCP or TCP, the compounds formed at elevated temperatures:

It was found that *stability* and *solubility* of calcium phosphates decreases by orders of magnitude with increasing *pH* of aqueous solution at constant temperature (Fig. 2-22). This is caused by the fact that orthophosphoric acid is weak and when the pH is lowered, the PO₄³⁻ ions are progressively combined with protons to form HPO₄²⁻ or H₂PO₄⁻ ions [139].

Hydroxyapatite, the most stable calcium apatite (for $\text{pH} > 4.2$), was found to be extremely susceptible to this phenomenon. Consequently, the most stable calcium phosphate in more acidic solutions ($\text{pH} < 4.2$) is dicalcium phosphate dihydrate (DCPD).

Fig. 2-22: Solubility diagram for the system $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ at ambient temperature [139]

Calcium apatites, a subgroup of calcium phosphates, are variable structures predisposed to substitutions of many atoms. These substitutions induce changes in lattice parameters while initial apatite skeletal framework is retained. Chlorine, fluorine and hydroxyl group (OH^-) are the most common substitutes (resulting in chlor-, fluor- and hydroxyapatite, respectively). Due to its bioactive nature and close resemblance to mineral phase in bones and teeth, hydroxyapatite (HA) has become a key substance during the last decades [140-153].

2.2.2.2 Hydroxyapatite

Hydroxyapatite is a naturally occurring form of calcium apatite. The name apatite derives from a Greek word “apatao”, which means “I am misleading” and refers to its easy confusion with similar appearing gemstones. It is an opaque, vitreous mineral, naturally white, but it can also have grey, yellow or greenish coloration (Fig. 2-23).

The density of hydroxyapatite is indicated as $\rho = 3.156 \text{ gcm}^{-3}$ and its molecular weight is $m_a(\text{HA}) = 502.31$. As other apatites, its hardness at Mohs hardness scale is 5, i.e. harder than

fluorite, Pt or Fe and softer than orthoclase feldspar or Ti. Basic properties of mineral HA are given in Table 10.

Fig. 2-23: Opaque whitish angular crystals of hydroxyapatite [154,155]

Table 10: Basic characteristics of mineral hydroxyapatite [135,136]

Property	Typical value
Density	3.156 gcm ⁻³
Molecular weight	502.31
Mohs hardness	5
Tenacity	brittle
Optical isotropy	uniaxial
Index of refraction (ω)	1.651
Index of refraction (ϵ)	1.644
Birefringence	0.007
Luster	vitreous to dull
Diaphaneity	transparent to opaque

Stoichiometric formula of crystalline hydroxyapatite is $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, but is usually indicated as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ to denote that the unit cell comprises two molecules.

HA crystallizes in *hexagonal-dipyramidal system* with a space group P63/m. Its cell dimensions are mostly indicated as $a = b = 0.9418 - 0.9423 \text{ nm}$ and $c = 0.6880 - 0.6884 \text{ nm}$ (i.e. ratio $a:c = 1: 0.731$ and unit cell volume is 0.5276 nm^3). HA crystallizes as short to long hexagonal prisms ([0001] planes) or thick tabular crystals ([0001] planes). For pure HA, the relative intensities of the three major peaks in X-ray spectroscopy diffraction pattern are 100% (at $d = 2.814$, $\theta = 31.773^\circ$) and 60% (at $d = 2.778$, $\theta = 32.196^\circ$ and $d = 2.720$, $\theta = 32.902^\circ$).

The structure of hydroxyapatite is complex [156]. Fig. 2-24 shows the 3-dimensional structure of hydroxyapatite structure plotted in software ATOMS.

Fig. 2-24: Isometric view of hydroxyapatite structure

Two crystallographically independent calcium atoms could be found in the unit cell of the HA. Calcium atoms of the first type (denoted as Ca₁) are surrounded by six oxygen atoms, forming a distorted octahedron. Atoms of the second type (denoted as Ca₂) are surrounded by six oxygen atoms belonging to PO₄ groups and two oxygen atoms belonging to hydroxyl (OH) groups. Phosphorus atoms are surrounded by four oxygen atoms in a compact tetrahedron. The network of PO₄ tetrahedra provides skeletal framework that gives stability to the apatite structure.

Chemically HA *resembles the mineral phase of bones* or tooth enamel, making it an attractive biomaterial choice [157-160]. As compared to synthetic HA, natural apatites contained in biological tissues are calcium deficient and there are minor differences in stoichiometry, composition and crystallinity (Table 11).

Synthetically produced HA usually retain higher *crystallinity ratio* than HA in biological tissues. The ratio is *determined by the production process and prospective heat treatment* (mainly annealing temperature and time). High levels of crystallinity of synthetic HA are beneficial for long-term survivability and proper functional life of implant in service [3] while

high resorbability of the amorphous phase and a presence of metastable phases are useful for accelerated implant fixation and promotion of faster bone remodeling.

Table 11: Conformity of synthetic hydroxyapatite with bone and tooth enamel [161]

Property	Synthetic HA	Bone tissue	Tooth enamel
Ca/P ratio	1.67	1.65	1.62
Crystallinity	> 80%	33 - 37%	70 - 75%
Unit cell a-axis	0.9422 nm	0.9419 nm	0.9441 nm
Unit cell c-axis	0.6880 nm	0.6880 nm	0.6882 nm
Chemical composition [%]			
Ca ²⁺	39.60	24.50	36.00
P ⁵⁺	18.50	11.50	17.70
Mg ²⁺	traces	0.55	0.44
K ⁺	traces	0.03	0.08
Cl ⁻	-	0.10	0.30
F ⁻	-	0.02	0.01
CO ₃ ²⁻	-	5.80	3.20

The extensive usage of hydroxyapatite in modern hard tissue replacement surgery originates in its *excellent biocompatible properties*. Bioactive HA coatings on metallic implants have been reported to [162]:

- promote earlier stabilization of the implant in the surrounding bone, supporting the bone in-growth and improving the implant-bone bond strength
- decrease the release of metallic ions from the implant, reducing the possibility of intoxication in vascular system and subsequent health hazards
- shield the surface of the prosthesis substrate from environmental attacks, facilitating long-term function performance and lowering the risk of substrate failure in load bearing applications
- extend the functional life of an implant as compared to cemented implants

Adverse clinical results of HA have also been reported: decrease in the chemical stability of the coating and increase in its degradation due to formation of metastable phases. However, HA still remains the most sought-after compound for all hard tissue replacement applications.

2.2.2.3 *Titanium dioxide*

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium. Natural titanium dioxide occurs in three forms: rutile, a tetragonal mineral of

prismatic habit, often twinned; anatase (also known as octahedrite), a tetragonal mineral of dipyramidal habit and brookite, an orthorhombic mineral. Anatase and brookite are relatively rare minerals and the titanium dioxide crystals are mostly composed of rutile, which has the lowest molecular volume of the three polymorphs.

The name *rutile* is derived from a Latin word “rutilus”, “reddish”, in reference to the deep red color observed in some specimens when viewed by transmitted light. It is an adamantine mineral found in metamorphic rocks, pegmatites or basic magmatites. Its diaphaneity ranges from transparent to translucent at thin edges and it can be found in variety of colors: blood red, bluish, brownish yellow, brown red or violet. Rutile occurrences in nature are never pure; it is found with contaminant metals such as iron. It is commonly found as golden acicular crystals inside quartz crystals, a structure known as “rutilated quartz” or “rutilite” (Fig. 2-25).

Fig. 2-25: Various forms of rutile crystals

The density of rutile is indicated as $\rho = 4.250 \text{ gcm}^{-3}$ and its molecular weight is $m_a(\text{rutile}) = 79.88$. Its hardness at Mohs scale is 6 - 6.5, i.e. harder than hydroxyapatite, pure titanium, window glass or knife blade and softer than quartz or hardened steels. Basic properties of mineral rutile are given in Table 12.

Stoichiometric formula of pure titanium dioxide is TiO_2 . As well as hydroxyapatite, the titania crystal unit cell comprises two molecules.

Titania (rutile) crystallizes in *tetragonal-ditetragonal dipyramidal system* with a space group $\text{P4}_2/\text{mm}$. Its cell dimensions are mostly indicated as $a = b = 0.4594 \text{ nm}$ and $c = 0.2958 - 0.2959 \text{ nm}$ (i.e. ratio $a:c = 1:0.644$ and unit cell volume is 0.0062 nm^3). Generally, titania

commonly crystallizes as prismatic, often slender to acicular crystals ([001] planes), or massive granular crystals. For pure titania, the relative intensities of the three major peaks in X-ray spectroscopy diffraction pattern are 100% (at $d = 3.245$, $\theta = 27.446^\circ$), 50% (at $d = 1.687$, $\theta = 54.322^\circ$) and 41% (at $d = 2.489$, $\theta = 36.085^\circ$).

Table 12: Basic characteristics of mineral rutile

Property	Typical value
Density	4.250 gcm ⁻³
Molecular weight	79.88
Mohs hardness	6 - 6.5
Tenacity	brittle
Optical isotropy	uniaxial, strongly anisotropic
Index of refraction (ω)	2.605 - 2.613
Index of refraction (ϵ)	2.899 - 2.901
Birefringence	0.294
Luster	adamantine, metallic
Diaphaneity	transparent, translucent on thin edges

The structure of body-centered titania unit cell is simple: all titanium atoms are equivalent, each of them encapsulated in a regular octahedron consisting of six oxygen atoms. Fig. 2-26 shows the 3-dimensional structure of titania structure plotted in software ATOMS.

Fig. 2-26: Isometric view of rutile structure

As a two component compound, TiO₂ is commonly contaminated with impurities such as Fe, Ta, Nb, Cr, V or Sn. The chemical composition of titania could be seen from Table 13.

Table 13: Chemical composition of TiO_2

Property	Synthetic TiO_2
Crystallinity	manufacturer dependent
Unit cell a-axis	0.4594 nm
Unit cell c-axis	0.2958 nm
Chemical composition [%]	
Ti^{4+}	59.94
O^{2-}	40.06
Fe^{2+} , Fe^{3+}	traces
Ta^{5+}	traces
Nb^{4+} , Nb^{5+}	traces
Cr^{3+}	traces
V^{5+}	traces
Sn^{4+}	traces

The *application range* of rutile is almost limitless. Due to its brightness and high refractive index (Table 12), it is often used as opacifier to provide whiteness and opacity to products such as paints, coatings, plastics, papers, inks, foods (food coloring E171), medicines (pills and tablets) as well as toothpastes. When deposited as a thin film, it makes an excellent reflective optical coating for sunscreens, dielectric mirrors and some gemstones.

Being a novel material in biomaterials science, titania is a likely *candidate to replace hydroxyapatite* for hard tissue replacement coatings [163]. Recently, titania coatings were proven to facilitate osseointegration, i.e. creating a direct structural and functional connection between living bone and the load-bearing artificial implant. Also, titanium dioxide in solution or suspension can be used to cleave protein that contains the amino acid proline at the site where proline is present (a breakthrough in cost-effective protein splitting). Preliminary osteoblast cell cultures experiments demonstrated that HVOF deposited nano-structured titania coatings supported osteoblast cell growth and did not negatively affect cell viability.

Thermal spraying of titania coatings onto metallic (Ti-6Al-4V) substrates for biomedical usage has not been covered in the literature thoroughly. This research aims to be one of the pioneering works in providing the necessary experimental data on deposition of titania coatings and subsequent coating properties.

CHAPTER 3: EXPERIMENTAL SETUP

This chapter describes the thermal spray and measurement devices used as well as methodology and experimental approaches used in the work. Additional descriptions and related settings and measurements could be found in Appendix A.

A flowchart of all experimental investigations carried out within this study is appended:

Fig. 3-1: Flowchart of experimental investigations

In the first part, a description of the two *thermal spray systems* used in the study is provided and particular thermal spray parameters selected for the study are introduced.

In the next part, the *experimental layout* is described. As described in section 1.2, the work is divided into two main parts: a study of influence of selected thermal spray parameters on in-flight properties of powder particles and a study of influence of in-flight properties (temperature and velocity) on the properties of resulting coatings. The former was carried out according to two different experimental approaches (One-at-a-Time, Taguchi design) and their details are provided as well as details of a regression analysis of the results obtained from the two methods. The latter research encompasses various methods of coatings characterizations; their respective details as well as details of some complementary measurements are provided.

Last part of this chapter describes the *software simulations* performed in order to obtain results alternate to the results acquired by experiments.

3.1 Thermal Spray Devices

3.1.1 Atmospheric Plasma Spray System

General working principles of plasma spray method was described in section 2.1.2.5. *Atmospheric plasma spray* employed in this study was operated using Computerized Plasma/HVOF Control Module System model 4600 (Praxair, Inc., Danbury, USA). Detailed description of the system and attached modules is provided in Appendix A. The integrated closed loop control function of the Control Module should ensure the *uniformity of the plasma jet properties* for consecutive runs under the same spraying parameters. To identify the functionality of the closed control loop function and to determine the *stability and repeatability* of the process under given set of conditions, an experiment was carried out (Appendix A).

As a *primary arc gas*, purified *argon* was used. Argon was also used as a carrier gas to carry the powder from the feeders into the jet. Purified *helium was used as a secondary gas*, purchased from Soxal, Pte. Ltd., Singapore (specifications provided in Appendix A). Advantages and disadvantages of argon and helium as primary and secondary gases, respectively, were discussed in chapter 2.1.2.5.

It was found (Appendix A) that the powder feedrate controller does not operate well in *grams per minute mode* (GPM). More stable *revolutions per minute mode* (RPM) mode was used instead. To provide a transparent transfer conversion between the employed RPM mode and the GPM mode commonly used in the research, an additional experiment was carried out.

The total powder feedrate in the RPM mode is influenced by two factors: revolutions of the powder wheel at the base of the canister and the actual flow of carrier gas into canister. The two influences were specified also specified (Appendix A).

The *plasma gun* used for all measurements was Praxair's *SG-100* [164], equipped with internal 10°-angle feeding anode. The SG-100 gun was mounted onto IRB 2400 M96 *robotic arm* (ABB Robotics Products AB, Ltd., Zurich, Switzerland).

3.1.1.1 Selected plasma spray parameters

The influence of various factors on the resulting plasma jet properties was described in section 2.1.2.5. Among all, the properties of the jet (e.g. gases temperature and velocity, amount of powder entering the jet, etc.) are controlled by the *plasma spray parameters* (PSP) as set in the system control module. Around 140 parameters can be set in the system console. To study the influence of the system settings on the plasma jet and, consecutively, in-flight particle properties, the following *six parameters of crucial importance were selected*.

With constant power input, the energy of the plasma can vary over time due to minor changes in the arc caused by fluctuating arc conditions (e.g. anode or cathode material ablation, roughening and minute oxidation or changes in metallurgical composition). The *net power* (net energy, NPW, unit: kW) function regulates the closed loop control function of the plasma energy by changing the DC power input instantly. It reacts to the changing physical conditions, automatically adjusting the spray parameters to maintain a constant powder heating region. Generally, increase in net power gives rise to jets of higher temperature and velocity. The relative increase of the two respective properties is important: higher plasma jet temperatures transfer more heat to the powder particles, however, the higher velocities result in shorter dwelling times in the jet and, subsequently, reduced heat transfer.

Main arc gas flow (main gas flow, MGF, unit: scfh) is an important factor influencing both the plasma jet temperature and velocity. Higher main gas flow is expected to give rise to higher velocities of the particles. Main gas is partially used for cooling the SG-100 gun.

Auxiliary arc gas flow (secondary gas flow, AGF, unit: scfh), used for additional stabilization of the plasma arc is usually lower than the flow of main gas and is therefore expected to have a lesser impact on the in-flight particle properties.

The effects and potential issues of various levels of *carrier gas flow* (CGF, unit: scfh) were described in 2.1.2.5. Flow of a carrier gas contributed to the total flow of gases in the plasma gun orifice.

Linked to the carrier gas flow parameter, *powder hopper revolutions per minute* (hopper revolutions, RPM, unit: 1) influence the amount of powder entering the plasma jet. As described in 2.1.2.5, increase in the amount of powder entering the jet could lead to decrease in average temperature and velocity of the particles, respectively.

Last factor selected for investigation technically does not belong to PSP as it is not directly set by the system control module. However, due to a presence of steep space gradients in temperature and velocity (2.1.2.5), *spray distance* (stand-off distance, SPR, unit: mm) is one of the key factors influencing the powder particles dwelling time in the jet and determines the amount of heating and acceleration the particles undergo.

3.1.2 Cold Spray System

General working principles of cold method was described in chapter 2.1.2.6. The *cold spray experiments in this study* were carried out using cold spray system designed and manufactured at Institute of Theoretical and Applied Mechanics, Russian Academy of Science (Siberian Department of RAS, Novosibirsk, Russia). More detailed description of the system components is provided in Appendix A.

In this study, compressed air was used as the *pressure and feeder gas*, respectively. The maximum working pressure of the compressed air in the supplying pneumatic system was 2.5 MPa. To aid the powder feeding into the nozzle, the pressure gas was retained at lower pressures as compared to the feeder gas. The difference in both pressures resulted in additional powder intake into the nozzle. The *Laval nozzle* used in this study was fabricated from wear-resistant ceramics and attached onto an IRB 4400 *robotic arm* (ABB Robotics Products AB).

3.1.2.1 Selected cold spray parameters

Much like in plasma spraying, the most influential factors determining the properties of the cold spray jet and subsequently the in-flight properties of the powder particles are the *cold spray parameters* (CSP), adjustable in the control panel of the main module. As the system used does not allow entering fully manual mode, the total number of controllable parameters is

lower than that of plasma spray. The parameters that were not studied were held at constant values for all the measurements: a powder feedrate motor frequency (equivalent of the feedrate, 50 Hz), spray distance (100 mm from the substrates) and nozzle translational speed (60 mm s^{-1}). To study the influence of CSP on the cold spray jet and, consecutively, in-flight particle properties, the following *five parameters were selected*.

The *temperature in the pre-heating chamber* (temperature of the pressure gas, TPG, unit: K) is adjusted by an electric current in the furnace circuit. As described in 2.1.2.6, pre-heating of the pressure gas is used to aid in particle deformation.

The *pressure of the working gas* (PWG, unit: MPa) is the pressure of the gas flowing through the pre-heating chamber. The higher the pressure, the higher the gas flow velocity and, subsequently, higher resulting velocity of the particles. Increase in velocity (i.e. kinetic energy) is expected to give rise to coatings with inferior porosity and higher adhesion levels.

The *pressure of feeder gas* (PFG, unit: MPa) is the pressure of the gas flowing through the powder feeder unit and gathering the powder from the rotating shaft.

The choice of *substrate material* is an important factor in terms of e.g. splashing behavior of the splats or coating adhesion. Two different substrates were used for the production of the coated samples: Ti-6Al-4V biomaterial alloy and common vitreous glass.

The last factor under study for the cold spray experiments was the *number of nozzle passes* (NOP, unit: 1). The number of passes is directly proportional to the resulting coating thickness. As described in 2.1.3, the prospective coating build-up is not guaranteed after the deposition of the first layer. The resulting thickness after various numbers of passes would therefore serve as an efficiency indicator.

As the powder particle in-flight properties measurements were not carried out for the cold spray system, the values of the *five investigated parameters were not systematically changed* according to an experimental layout. Instead, the values were selected based on trial experiments carried out using ceramic powders of similar properties. Every cold spray deposited sample was therefore produced by alteration of all investigated spray parameters.

The cold spray *system stability and reliability* could not be accurately determined due to the absence of the particle in-flight properties measurements.

3.2 Experimental layout & methodology

The experimental work within this study was divided into two main parts: the study of influence of plasma spray parameters on the in-flight particle properties (average temperature and velocity profiles, 3.2.1) and the study of some selected properties of the deposited coatings (3.2.2).

3.2.1 *Particles In-flight Properties Measurements*

The first focal point of the study is the specification of the PSP influence on the particle in-flight temperature and velocity, the two most impacting factors in terms of final coating properties. To determine the two characteristics at different distances from the plasma gun, fast-shutter optical diagnostics system was used (3.2.1.1).

The layout of all experiments was set according to two statistical approaches used to evaluate the influence of the spraying parameters on the powder particles in-flight properties. “Several parameters, one-at-a-time” method (One-at-a-Time, OAAT, 3.2.1.2) is ranked among basic approaches in studying processes influenced by external parameters while more advanced “Taguchi design of experiments” approach (3.2.1.3) requires advanced knowledge of statistical principles in order to plan the experimental schedule and evaluate the results.

Additionally, a regression analysis of the results (3.2.1.4) was aimed at determining the type of relation between particular PSP and powder particles in-flight temperature and velocity, respectively. Discovered types of relations were precisely stated by calculating respective coefficients and constructing a set of governing equations concluded the obtained findings.

3.2.1.1 *In-flight Measurements*

Various techniques of capturing high-velocity process images have been developed. Using a fast-shutter optical system, stroboscopic light generated by conventional laser sources and a PC unit capable of real-time processing and interpretation of the measured results, these methods (generally called “*Particle Image Velocimetry*”, PIV) are based on measuring of flow-fields seeded with small particles and provide a unique insight into high-temperature or high-luminosity industrial processes. Among the monitored parameters of interest in the plasma spray process are spatial particle distribution, particle velocity distribution and particle temperature distribution fields [165,166].

Formerly, the instruments provided solely point diagnostic from the jet, often causing misinterpretation of the results (e.g. changing background radiation due to bursts of plasma or illusive fumes of the powder material). The new generation of the two-dimensional CCD-chip cameras of reasonable cost and sufficient time resolution are not sensitive to any anomalies in the spray pattern. The state-of-the-art PIV methods can be divided into two groups according to the way the information is obtained from the process [166]:

1. *Passive Image Spray Monitoring* (PISM)

The term passive refers to the fact that the self-radiation of the particles in the process is used. This type of image capturing allows obtaining visual overviews of the entire spray jet in combination with a quantitative evaluation of the spray properties from selected regions of the spray jet, providing more reliable indication of the trends within the process. A typical representative of PISM method is a two-color pyrometry for measuring particle temperatures.

2. *Active Image Spray Monitoring* (AISM)

Basic concept of active spray monitoring is illuminating the process using an additional source of light. Short consecutive pulses of a single wavelength coherent laser light are mostly used (Nd: YAG). The emitted laser light is shaped into a form of two-dimensional sheet and projected towards the process. Retaining the same wavelength as the incident laser source, the resultant light scattered at the particles is then recorded. The main advantage of AISM methods is disregarding the brightness coming from the process (such as the plasma jet), allowing the reception of measured data independently on the measurement background. A typical representative of AISM method is the laser-assisted cold spray process particle velocity measurement.

Presently, the innovated and improved PIV methods such as super-resolution PIV, high frame rate PIV or stereoscopic PIV are used in specialized studies [167].

In this study, *SprayWatch 2i* (Oseir, Ltd., Tampere, Finland) diagnostics system was used. SprayWatch is a PISM optical system that uses a high-resolution 12-bit fast shutter CCD array camera to create digital images of the spray and measures the particle properties in-situ. The great number of sensors embedded in the CCD chip makes SprayWatch extremely sensitive to the changes in particle in-flight properties.

Digital images taken with short exposure times to stop the high-speed particles are processed by algorithms identifying individual particles in the images. For measurement of the particle *velocity*, SprayWatch uses a *time-of-flight method*. The length of a particle trajectory on the CCD detector is measured and is then converted to velocity by dividing by known camera shutter time. For a typical plasma spray process, the shutter times vary from 5 – 30 μ s [168].

Simultaneously, the camera takes additional images using longer exposure times to measure the average particle temperatures in the spray using *two-color pyrometry*. An optical double-stripe filter is integrated in the camera and covers part of the CCD detector. The image of the spray passes through the filter and is imaged on the CCD in two different wavelength ranges. The radiation of the particles is integrated during the specified shutter time. The detected intensity is a sum of radiation of all particles passing through a camera measurement volume during the integration time. The distribution of the average particle temperature in the spray can then be calculated using calibration information [169].

The SprayWatch camera was set perpendicularly to the plasma jet axis to measure the average temperature and velocity of the particles in the geometrical middle of the jet at various spray distances (Fig. 3-2). As the particles traveling in the middle of the jet have temperatures and velocities higher than the particles traveling on the periphery of the jet, the measurement volume for all experiments was set to *cover the entire height of the plasma jet at a given spray distance*. The reliability of the measurement was therefore improved as any potential change in the particle in-flight properties due to an influence of any PSP would be reflected as a change in value averaged from all particles within the jet.

For particular measurements, the focus distance and camera lens aperture (and subsequently the size of the measurement volume) were adjusted according to the specific needs (Appendix A) as well as shutter times and some controllable software features (gain, binning). To ensure results uniformity and minimize the influence of the measurement error, trial runs of all combinations for both powders were conducted prior to main measurements to find out optimal SprayWatch settings. Table 14 summarizes the settings of the SprayWatch system for the measurements of the in-flight particle properties of both HA/TiO₂ powders for

OAAT and the Taguchi methods, plasma system stability measurements (Appendix A) and fatigue life experiments, respectively.

Fig. 3-2: SprayWatch unit setup [168]

Table 14: SprayWatch system settings in manual mode (HA/TiO₂)

Software variable		One-at-a-Time & Taguchi	Plasma system stability	Fatigue life experiments
Focus distance	[mm]	245 / 250	235 / 250	235 / 250
Aperture	[%]	80 / 40	100 / 80	100 / 40
Gain		high / high	high / high	high / high
Shutter time, velocity	[μs]	15 / 15	15 / 15	20 / 15
Shutter time, temperature	[μs]	200 / 200	500 / 200	200 / 200
Horizontal binning		false / false	true / false	true / false
Vertical binning		false / true	false / false	false / true

Due to its high brightness and high refractive index (2.2.2.3), the measurements with TiO₂ powder have been carried out with lowered camera aperture values, resulting in a bigger depth of focus as compared to the measurements with pale HA powder of low reflexivity. The camera focus distance was adjusted based on trial runs and results of the measurements of the spray width at different spray distances (3.2.2.1). Trial runs of the plasma spray process determined the longest possible focus distance in order to allow the camera to detect the particles (CCD resolution constraint) while the experiments with spray width for different PSP

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combinations determined the shortest focus distance in order to detect all particles within the jet (minimum measurement volume constraint).

SprayWatch real-time analysis software works in two modes. In fully automatic mode all the parameters affecting the capturing process (i.e. camera shutter times, aperture, gain levels, triggering, etc.) are controlled by the system to obtain best images quality. In this mode, the system changes all the parameters instantly to capture the highest number of particles. It was found that the SprayWatch *algorithms for automatic mode did not work properly* and it was therefore decided to *use the manual measurement mode*. In this mode, the parameters are controlled by the user (usually fixed during a single measurement) and stored in *profile files* [168,169]. In contrast to the automatic mode the number of captured particles is lower due to the impossibility to adjust the system according to the current situation. However, the *uniformity of the results is retained* and consequently their mutual comparability.

All measurements of powder particle in-flight properties were performed for *at least 2 minutes* for every combination of PSP. The values obtained from the first 15 s after the start of the deposition process were not considered due to plasma jet initial stabilization. Measured data points of temperatures and velocities were average values of all detected particles within 20 s intervals. Such data points were recalculated and displayed every 5 s. The averaging of the measured values improved the measurement reliability by suppressing the effect of any abrupt event (e.g. plasma jet burst, powder choking and sudden release in the carrier hose).

Testing of the SprayWatch system results stability was performed. It was found the *reliability of the results measured using the SprayWatch CCD camera is good*. Anticipated variations of measured data were higher for HA powder, in accordance with experiments on plasma source stability (Appendix A).

Hi-Watch laser illumination system was attached to the measuring unit to extend the measuring capacity of the CCD camera, to increase the reliability of the experimental results and to compensate for the lower number of detected particles in the manual mode. *Hi-Watch* (Oseir, Ltd.) is a high-power diode laser stroboscope system [168] that can be used to illuminate the measurement volume of SprayWatch to detect small, high speed targets, facilitate particle detection under strong background radiation or to detect particles in cold

processes such as cold spray, grit blasting or shot peening, which cannot be detected solely by SprayWatch.

Hi-Watch fires (by default) three consecutive laser pulses and the *automatic particle detection algorithm* detects the three particle images generated. Each of the three images is binarized and the algorithm then searches for any three particle data points matching a linear trend inclusive of a preset error value. The detection algorithm can be optimized by adjusting the pulse parameters (pulse durations, intervals between pulses and numbers of consecutive pulses), the size of the area for detecting the three data points and the error value.

Trial experiments were conducted to find *optimal settings of the Hi-Watch laser* parameters in order to facilitate superior in-flight particle monitoring. The parameter values used in measurements are shown in Table 15. As both HA and TiO₂ powders have different optical reflexivity, their respective optimal Hi-Watch parameters values differ slightly.

Table 15: Hi-Watch system optimal parameter settings for HA and TiO₂ powders

Parameter		HA	TiO ₂
Pulse current	[A]	60	40
Number of pulses		3	3
Single pulse duration	[μs]	0.50	0.75
Interval between pulses	[μs]	1.00	1.00

Additional experiment was conducted to detect the influence of Hi-Watch integration on the measured data (Appendix A). The results showed the differences in values measured by SprayWatch system only and Hi-Watch laser assisted SprayWatch are relatively small and fall within the error range of the plasma system. Furthermore, no explicit trend in the differences between the two measurement methods was found and the credibility of the SprayWatch measurements was retained after Hi-Watch system integration.

3.2.1.2 One-At-A-Time Method

The principle of “*Several parameters, one at a time*” method (OAT) consists in *changing the values of one parameter while keeping the rest of the parameters at constant values* [170-182]. The evaluated parameter is changed within a carefully chosen range. The choice of parameter value step and range span is essential: too wide gap between adjacent levels of the parameter could lead to loss of information (e.g. bypassing any nonlinear effects

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such as carrier gas phenomena) and too narrow range could cause the parameter’s influence to remain undisclosed.

The major advantage of OAAT method is its *accurate determination of a respective parameter’s effect* on the characteristics of the plasma jet and subsequently the in-flight properties of the powder particles. Relative simplicity of statistical processing of this method makes it a preferred choice among other techniques. However, revealing the trends of respective influences by this method is resources and time consuming. Furthermore, the principles of OAAT do now allow detecting any potential interactions of the acting parameters, i.e. alterations in particle in-flight properties due to joint incidence of more parameters.

A layout of experimental work according to OAAT method could be seen from Table 16. *Measuring ranges and step increments of the six chosen PSP (3.1.1.1)* are provided as well as their respective fixed values used in measurements of other parameters influences. The values were chosen according to previous tentative series of experiments and are valid for both investigated powders, i.e. HA and TiO₂.

Table 16: PSP ranges, steps and fixed values for OAAT experimental design

Plasma spray parameter	Unit	Measuring range	Step	Fixed value
Net power	kW	7 - 15	1	15
Main gas flow	scfh	40 - 100	10	100
Auxiliary gas flow	scfh	20 - 80	10	80
Carrier gas flow	scfh	6 - 15	1	12
Hopper revolutions	1	1 - 4	0.5	3
Spray distance	mm	75 - 150	12.5	100

Initially, 10 levels of each parameter were chosen per its respective range. Due to various technical limitations of the system (safety concerns, admissible system settings, etc.), the number of levels of some parameters was changed eventually.

The previously conducted experiment on plasma source stability (Appendix A) showed the system used in this study has a high stability considering the characteristics of the generated plasma jet. It was therefore decided to *reduce the number of repetitive measurements* at every given level of each PSP combination to 2. The arithmetic mean of the two runs was considered the measured value. In total, 94 trial runs were conducted according to OAAT design.

As plotting of changes in the in-flight properties within one measurement would not be transparent, *average values for each level of the six parameters* will be plotted and the minor changes will be incorporated as respective standard deviations.

3.2.1.3 Taguchi Design of Experiment

The fundamentals of OAAT method do not allow detection of interactions of the factors. As such interactions are likely to occur in plasma spray, it was necessary to implement another experimental method. “*Taguchi design of experiment*” technique was chosen as a suitable experimental technique to accomplish this task [178-181,183-186].

The Taguchi design of experiment (DOE), introduced in late 1940s by Dr. Genichi Taguchi belongs to a group of statistical concepts used in the area of product quality assessment and improvement. In general, it is a series of *three major steps* for evaluating of a process and understanding of the process overall performance.

1. Planning phase

In this phase, the intended *experiment setup* is designed with respect to the number of factors, number of levels per each factor, the anticipated mutual bonds, results reliability and variations or repeatability of the process.

In a common design of experiments, the number of necessary trial runs rises considerably with the number of factors and the number of levels per every factor. For instance, conducting an experiment with six three-level factors requires 729 trial runs. The statistical concept of the Taguchi’s design significantly reduces this number by effectively combining the individual factor levels, resulting in *high efficiency of the experimental design*. In a method known as *partial-factorial design* [186], Taguchi constructed a set of general designs, based on so-called orthogonal arrays. The term orthogonal indicates the possibility of independent evaluation of respective parameters influences. Use of these arrays aids in the determination of the least number of necessary trial runs in order to provide same amount of information as full-factorial designs (e.g. OAAT).

For the case of six three-level factors (used in this study), the corresponding standardized orthogonal array is L-18 (L_{18}). Following the L-18 design, the number of necessary trial runs is reduced from 729 to 18. As the L-18 orthogonal array was primarily designed for seven factors

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(six three-level and one two-level), the number of columns was reduced by one, forming a *custom orthogonal array*. The reduction could not be done at random as the original orthogonal array contains the information on factors mutual interaction and also assigning of the factors to the respective columns was restricted by certain statistical limitations. In this study, removing the two-factor column satisfied both the conditions. The modified L-18 orthogonal array with respective levels of chosen PSP could be seen from Table 17.

Table 17: Plasma spray parameters values for Taguchi experimental design

Trial run number	Net power [kW]	Main gas flow [scfh]	Auxiliary gas flow [scfh]	Carrier gas flow [scfh]	Hopper revolutions per minute [1]	Spray distance [mm]
1	7	40	20	6	2	75
2	7	70	50	10.5	3	100
3	7	100	80	15	4	125
4	11	40	20	10.5	3	125
5	11	70	50	15	4	75
6	11	100	80	6	2	100
7	15	40	50	6	4	100
8	15	70	80	10.5	2	125
9	15	100	20	15	3	75
10	7	40	80	15	3	100
11	7	70	20	6	4	125
12	7	100	50	10.5	2	75
13	11	40	50	15	2	125
14	11	70	80	6	3	75
15	11	100	20	10.5	4	100
16	15	40	80	10.5	4	75
17	15	70	20	15	2	100
18	15	100	50	6	3	125

2. Conducting phase

The mutual bonding of factors within a single measurement in Taguchi design brings along a potential risk of invalidating the entire measurement set by a single faulty trial run evaluation. As in OAAT measurements, it was therefore decided to conduct repetitive trials for each combination. The good plasma source stability (Appendix A) allowed *reducing the number of repetitive runs* to two. The total number of the Taguchi method trial runs was therefore 36.

To further improve the reliability of the experiments in Taguchi design, the trial runs were carried out in random order. The randomization of trial runs was performed for both repetitive runs for each combination of PSP (“*complete randomization*”). This precaution eliminates the influences of potential trends in measured particle in-flight properties [184,186].

3. Analysis and interpretation phase

The orthogonal arrays structure provides an opportunity to use multiple methods for evaluation of the results. *Two methods* were used in this study: *plotting method* and *analysis of variances*.

The former, comparable to the results provided by OAAT method, provides information on parameters influences on particle in-flight properties. The method averages values measured at each level of every PSP (i.e. 12 data points in this study) and *plots the averages as a sequence of points*. As each level generates one average point, three points were obtained for every PSP. The magnitude and character of a particular parameter influence is indicated by the slope of the resulting three-point diagrams. As Taguchi method includes basic factor interactions, some differences from OAAT method results were expected.

The latter method, also referred to as *ANOVA*, is a statistical, decision-making tool for detecting changes in average performance of measured data. By *comparing the variations of the data measured at different PSP levels with the overall variation changes*, ANOVA determines the credibility of measured data sets and respective factors influences. In addition, the percent contribution of each factor to the overall changes can be specified and the mutual interactions between factors can be determined.

To assess the results of ANOVA method, statistical *F-test* was performed. In F-test, the ratio of variance due to the effect of a chosen PSP and variance due to an error term (F-ratio) [184] is used to estimate the statistical significance of the investigated factor with respect to all factors included in the error term.

The F-ratio obtained from the analysis is compared with a value from a standardized F-table. The F-table values are given based on three variables: degrees of freedom (DOF) of a parameter variance, degrees of freedom of an error term and a confidence level. *Degrees of freedom* of the parameter variance is a number of PSP levels reduced by 1, i.e. 2 for three-level

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factors. Degrees of freedom of the error term is a total number of experimental runs reduced by a sum of PSP degrees of freedom and 1, i.e. 23 for six three-level factors in modified L-18 orthogonal array with two repetitions. The *statistical confidence level* is usually denoted as a percentage value representing a chance of error in results interpretation. Too low confidence level could result in a false interpretation of in fact unessential parameter influence. High confidence levels reduce this risk. However, too high confidence levels could lead to rejection of a significant influence of a selected PSP on the measured property. The standardized F-table for degrees of freedom 2 (PSP) and 23 (error term) and three chosen confidence levels (90, 95 and 99%) could be seen from Table 18.

Table 18: F-test table values for (2, 23) degrees of freedom [184]

Confidence level	90%	95%	99%
F-test value	2.94	3.42	5.66

The parameter and error variances of a selected PSP are recognized as unequal in case the calculated F-ratio is higher than the F-table value. In such case, the selected PSP is deemed to have a significant influence on the process at the given confidence level. This hypothesis is rejected when the calculated ratio is lower. The relative magnitudes of the calculated and tabulated F-ratio do not signify the extent of the influence of a selected PSP.

To better understand the influence of particular PSP on the in-flight temperature and velocity of powder particles, ANOVA results were used to determine a *percent contribution* of every PSP at the selected ranges.

For detection of *PSP interactions*, an adapted statistical method was used. Using the average values of measured properties at each level, a graphical plot of two-parametric curves was constructed for all 36 combinations of mutual PSP interactions. In each chart, three curves were plotted at each level of a selected PSP. Every curve included three data points for three levels of the second PSP under consideration. The difference in the slopes of the three curves determined the strength of the mutual interference of the two selected PSP [185]. Interchanging the sequence of the two parameters changes the curves but not their mutual slope directions and the possible interaction effects would be therefore revealed regardless of the PSP sequence.

Despite its advantages over general designs, the determination of single parameter's influence is less demonstrable in Taguchi design.

3.2.1.4 *Regression Analysis*

To complete the knowledge of PSP influences on powder particle in-flight properties, a mathematical method of results analysis was employed [187-189]. Based on *regression analysis of measured data* (from OAAT design), this method aided in revealing the nature of particular PSP - in-flight temperature or velocity relations and facilitated theoretical notation of the relations.

Basically, *four different types of mathematical relations were considered* for each of the 24 combinations:

Linear	$y = a + bx$	Eq. 4

Quadratic	$y = a + bx + cx^2$	Eq. 5

Exponential:	$y = ae^{bx}$	Eq. 6

Modified exponential:	$y = ae^{\frac{b}{x}}$	Eq. 7

where y denotes the measured in-flight temperature or velocity of particles, x denotes a value of the investigated PSP and a, b, c are the unknown coefficients to be determined.

Curve Expert software tool was used for experimental data fitting and respective coefficients determination. A *statistical method of least squares* is the most efficient and reliable method for data plot curve fitting and was used in this study [190,191].

The four types of relations were fitted onto the experimental data and the respective *residual plots* of measured data were calculated. A residual plot at a certain level of particular PSP represents the difference between the measured value (temperature, velocity) and the value derived from the model (evaluated from equations). The residuals provide an indication of the particular model's performance. Optimally, the residuals should exhibit a random scatter around zero, which indicates that the data points are randomly distributed around the curve. Long series of either positive or negative residuals indicate a better model for the data is likely to exist.

Goodness of curve fit was estimated using two quantities: the correlation coefficient and the standard error of the estimate. The correlation coefficient is a value from 0 to 1 and

describes the quality of the approximation, with a correlation coefficient of 1 being an optimal fit. The standard error is a positive value representing the data curve fit.

A linear dependence between the selected PSP and the resulting quantity (temperature, velocity) is the most likely relation type. Linear relation was therefore favored in the process of relation type determination. Quadratic relation between the PSP and particle in-flight properties signifies the *existence of an extreme value* (either minimum or maximum) for a given function and therefore the existence of an optimal or prominent parameter value. In such cases, the extreme values were calculated (temperature, velocity) as well as the respective level values of the PSP. Exponential and modified exponential trends are dependencies frequently observed for natural processes and were included to extend the span of the considered set of relation types. The existence of other types of relations is not impossible, it was, however, not investigated in this study.

In order to determine the most suitable theoretical relation type, *a standardized procedure was applied for the measured data* (Appendix A). In the next step, the respective equations were summarized including the calculated parameters.

Governing equations describing the entire process were constructed, involving *all six investigated PSP*. The relative percent contribution of all investigated PSP detected in Taguchi design were used for the calculations of *weighted averages* used in these equations. Furthermore, the disclosed *mutual interactions* obtained in Taguchi design were considered in the construction of the general equations.

The governing equations describing the plasma spray process together with the results obtained using OAAT and the Taguchi designs provide thorough and complete insight on the problems of PSP influence on powder particles in-flight properties. Such knowledge allows evaluation of the properties of the final coatings sprayed under given PSP conditions with respect to the most important in-flight characteristics of the particles, i.e. their temperatures and velocities.

3.2.2 Coating Characteristics Measurements

The second focal point of this study was the specification of the final coatings properties with respect to the previously measured in-flight powder particle properties (plasma spraying).

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Based on the results of the Taguchi design, *six different combinations* of PSP levels (denoted as PS-A, PS-B, etc.) were selected to represent the variances in the process of plasma spray. Four combinations correspond to extreme values of high/low in-flight temperature/velocity (PS-A, PS-B, PS-E, PS-F) and two combinations correspond to average values of both in-flight characteristics (PS-C, PS-D).

As the measured values of particle in-flight temperatures and velocities were found to be correlated to certain extent (5.2.1), the existence of distinct extreme data points (e.g. high temperature and low velocity) was rare. In such cases, the data points closest to the desired extreme combinations were selected. It is important to note that each of the six combinations correspond to a different Taguchi PSP set for HA and TiO₂ powders as the powders exhibited different in-flight properties under same PSP combinations.

The experimental sample coatings were deposited onto commercially available *Ti-6Al-4V substrates*. The substrates were electric wire-cut from a sheet using a programmable CNC device to achieve uniform dimensions and weight. The electric wire cutting method should also prevent induction of stresses into the substrate and ensure smooth and straight substrate edges. The standard dimensions of the substrates were measured as 29.08 x 24.11 x 2.64 mm (length x width x thickness) with the calculated standard deviations reaching 0.07 x 0.03 x 0.02 mm. The typical sample weight was 8.01 ± 0.04 g. Subsequent measurement of EDX reliability (Appendix A) has shown that the Ti-6Al-4V used was a high quality alloy conforming to the ASTM F136 Grade 5 standard.

To facilitate superior coating adhesion, the *substrates were grit blasted* [22,186,192] using Trinco (Trinco Trinity Tool Company, Co., Fraser, USA) Master 48 x 36 Cabinet sand blast device. To ensure *uniformity of the grit blasting process*, all specimens were grit blasted under uniform grit blasting conditions (Appendix A).

Different substrate geometries were used for basic coating characteristics (3.2.2.1), adhesion (3.2.2.6) and fatigue experiments (3.2.3.1), as described in the respective sections. All the *used substrates were held at ambient temperature prior to the deposition process* and no cooling of the substrates was applied during the spraying.

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As described in 3.1.1, a robot system was used for the coating deposition process (robot settings given in Appendix A). The number of torch passes for production of the samples was chosen as 15 for HA and 10 for TiO₂ powders, respectively. In applications where uniform coating thickness of the samples was required, the exact number of torch passes was chosen based on the results of thickness per pass measurement (3.2.2.1) and the powder feed conversion experiment performed (Appendix A). Spray distance was changed according to the chosen Taguchi combinations.

For each sample, the height of the robot arm step (a relative shift of the arm for spraying surfaces bigger than the width of the plasma jet) was chosen to ensure homogenous coverage of the substrate and obtain samples with flat surface and even coating thickness. The value of the step height was determined using an additional mathematical simulation: assuming normal distribution of the powder in the jet (in the plane perpendicular to the jet axis), the simulated torch passes were overlapped under different robot arm step heights and the total integral thickness of coatings was calculated. From the results, the optimal step height was determined. The optimal height of the robotic arm step is a function of the spray distance factor and the value was adjusted accordingly. The number of the robotic arm steps was chosen to ensure total substrate coverage even for the smallest step heights.

To ensure higher uniformity of the measured results, all specimens for each of the six combinations were sprayed together during one plasma spray run.

As the in-flight properties of particles were not determined for cold spray technique at the moment, the *experimental layout for cold spray parameters* (CSP) was composed in a different way. Five chosen CSP (3.1.2.1) were altered jointly, based on previous trial experiments with similar powders. A *total of six unique combinations of CSP* (denoted as CS-A, CS-B, etc.) were compiled for subsequent coated samples production (Table 19). Combinations CS-A to CS-D were cold sprayed using HA powder while for combinations CS-E and CS-F, TiO₂ powder feedstock was used.

The *Ti-6Al-4V substrates* used for cold spray experiments were identical with the substrates used for plasma spray and necessary surface modifications were also performed prior to the deposition. Additionally, *glass substrates* were used. Unlike the metallic substrates,

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the common laboratory grade glass sheets of 2.00 mm thickness were not modified and their surfaces were only chemically cleaned to remove oil, grease and impurities.

Table 19: Cold spray parameters values for cold spray experimental design

Cold spray parameter	Unit	CS-A	CS-B	CS-C	CS-D	CS-E	CS-F
Pressure gas temperature	K	533	523	533	673	533	524
Pressure of working gas	MPa	1.67	1.61	1.10	1.11	1.23	1.72
Pressure of feeder gas	MPa	1.72	1.71	1.19	1.21	1.35	1.89
Substrate material		Ti-6Al-4V	Ti-6Al-4V	glass	glass	glass	Ti-6Al-4V
Number of passes	1	5	10	1	1	1	5

No step increment of the robotic arm was applied for the production of samples using cold spray system. The successive passes of the Laval nozzle were carried out at identical areas of each of the substrates, resulting in narrow bands of coatings. The relative robot arm velocity was set to 40 mms⁻¹ for both powders and there was no artificial pause between the passes.

To investigate the produced coatings, several important *coating characteristics* were measured. Description of all experimental procedures is provided the following sections. In each section, a main description of the used *experimental devices* is provided. In Appendix A, respective *devices reliability and credibility* is estimated and some trial measurements are described to determine the stability and repeatability of the results.

3.2.2.1 Basic Coating Characteristics

A *width of the coating produced at different spray distances* was measured for both powders. For this purpose, a 600 x 50 mm Ti-6Al-4V bar was grit blasted and fixed in front of the plasma torch. The robotic arm carrying the gun was programmed to make 15 (HA) or 10 (TiO₂) passes across the width of the bar at the same location to create a band of coating. Subsequently, the arm moved by 50 mm along the bar length while increasing the spray distance by 15 mm at the same time. The plasma system settings for the width measurement could be seen from Table 20.

The width of the individual coating bands was then measured. The knowledge of the sprayed coating width at different spray distances was used for determining the SprayWatch CCD camera system focus distance to ensure measurement from the entire cross-section of the plasma jet (3.2.1.1) and setting of the height of the step or the robot arm to ensure even

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thickness of the coatings deposited onto the substrates. Preliminary runs of this experiment aided in selecting the spray distance measurement ranges for OAAT and the Taguchi design methods (75 – 125 mm) since it was difficult to obtain a good-quality coatings for very short and relatively long spray distances.

Table 20: Plasma system settings for coating width measurements

Parameter	Unit	HA	TiO ₂
Net power	kW	10	10
Main gas flow	Scfh	100	100
Auxiliary gas flow	Scfh	80	80
Carrier gas flow	Scfh	15	15
Hopper revolutions	1	3	3
Gun passes	1	15	10

The *thickness per pass of the plasma spray process* was measured [193,194]. To obtain a fundamental idea on the used plasma system’s deposition efficiency, HA and TiO₂ coatings were sprayed under two PSP combinations at two spray distances using two feedrates. As the increment in HA coatings was anticipated to be smaller, 20 transverse gun passes were carried out while 10 passes were carried out for TiO₂ powder (Table 21).

Table 21: PSP combinations for basic thickness per pass evaluation

Plasma spray parameters	Unit	1	2
Net power	kW	9	15
Main gas flow	scfh	60	100
Auxiliary gas flow	scfh	20	60
Feedrate		1	2
Carrier gas flow	scfh	15	18
Hopper revolutions	1	3	2
Distance		1	2
Spray distance	mm	75	125

The thickness of the samples before and after the deposition process was measured at 3 points for each of the 16 combinations and a thickness per 1 pass of the torch was calculated. The results were compared to the results of the powder feedrate conversion experiment (Appendix A) to obtain an idea on the loss of powder at different spray distances.

Following the basic thickness per pass investigations, an additional experiment was carried out. The six investigated samples (PS-A to PS-F) were sprayed with the same number of plasma torch passes (15 for HA and 10 for TiO₂, respectively) and the *thickness of the produced coatings was assessed* using different methods: micrometric screw measurements, optical microscopy and SEM. For flat anvils micrometric screw measurements, 10 measurements (5 before and 5 after spraying) were carried out at different parts of each sample (close to the four corners and in the geometrical centre) and an average value was determined. The samples for the optical and scanning electron microscopy were mounted into an epoxy resin, ground and polished, a process described in detail in 3.2.2.2. The coating thickness was then evaluated from the exposed cross-sections of the samples (5 measurements at 5 different cross-section points; the reliability of the SEM thickness measurements was increased by acquiring micrographs with at least 90% of the screen height covered by the coating).

The knowledge of the thickness of the coatings deposited under the six PSP combinations aided in determining of the exact number of passes to produce samples with coatings of similar thickness for experiments where this factor is essential (e.g. adhesion testing, fatigue life experiments).

Measurement of the thickness of cold sprayed samples using micrometric and optical microscopy methods could not be performed due to limitations in coating build-up. SEM thickness measurements of the cold sprayed samples were performed.

It is important to note that the standard weighing method of deposition efficiency measurement (i.e. amount of powder inserted vs. amount of coating produced) was not carried out in this study and the measurements of the thickness per pass and the total coating thickness are related indirectly to the deposition efficiency measurements.

3.2.2.2 Microstructure

To study the *microstructure of the produced coatings*, optical and scanning electron microscopies were used [195]. Both optical and SEM microscopes were precisely calibrated prior to observations (Appendix A).

The *profiles of the coating top-layers* (coating surface) were studied. The surfaces were covered by a 10 nm thick gold layer (details provided in Appendix A) and SEM micrographs

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(50 - 2000x) were acquired to assess the relative roughness of the sample surfaces, the top-layer splats splashing and morphology and the overall quality of the coating overlay. The optical microscopy images of the sample top-layers was not included in the results section due to an insufficient depth of focus of the optical microscopy.

Coating cross-sections were then prepared. The sprayed samples were cut using a diamond disc, mounted into two-component resin solids (resin M1201025, hardener M1201026, Struers, GmbH, Willich, Germany; resin to hardener ratio 1:2) and allowed to undergo proper curing (> 12 hours). The specimens were arranged in the resin so that the cross-sections contained an original, as-sprayed edge and an edge created by the diamond disc cutting. By subsequent mutual comparison of both edges, any potential effects caused by a delamination of the original edge, long-term exposure of the original edge to the ambient atmosphere or an effect of the cutting process would be assessed (e.g. different porosity levels). The mounted coated samples were then ground using SiC sand papers (gradual sequence of grades #180, #400, #800, #1200 and #2400, 90° sample rotation between steps) under decreasing pressure and increasing processing times. Rinsing of the samples in water and ultrasonic cleaning (5 minutes in ethanol) were performed between the grinding steps as well as optical microscope verification after each step. A 3 µm diamond paste was then used to polish the sample cross-sections. The polished samples were then covered by a 14 nm thick gold layer.

The polished sample cross-sections were investigated using optical microscopy and SEM at various magnifications. *Coating microstructure, splat shapes and morphology and a network of both horizontal and vertical cracks were studied.* Furthermore, the polished samples were used for coating top-layer relative roughness determination, verification of the uniformity of the grit blasting process, coating porosity evaluation, *interface adherence of coatings* to the substrates, coating thickness determination and EDX phase composition measurements.

The *cold spray coating top-layers* were investigated using optical microscopy and SEM under various magnifications. As well as the plasma sprayed samples, the top-layers of the cold sprayed samples were gold coated (14 nm layer) and the relative coating roughness, splats spreading behavior and the overall coatings quality were studied.

The *cold spray sample cross-sections* were prepared using procedure identical to the plasma sprayed samples and SEM micrographs were obtained. *The microstructure of the cross-sections was studied* as well as the substrate surface and coating top-layer roughness, coating thickness and EDX phase composition. Unlike the plasma sprayed samples, the porosity of the cold sprayed coatings could not be determined using SEM micrographs. Results of the performed optical microscopy of the cold sprayed samples cross-sections were not sufficiently transparent and are not included in this study.

3.2.2.3 Phase Composition

Two methods were used to determine the *composition of cold sprayed and plasma sprayed coatings*. Phase composition was measured using X-ray Diffraction Spectroscopy and the measured pattern were evaluated by Rietveld analysis [196-199]. The element composition was measured using Energy-Dispersive X-ray Spectroscopy.

The *X-ray diffraction spectroscopy* (XRD) method was used to study the changes between the initial powder feedstock and the produced coatings and the relative differences between the phase compositions of the coatings sprayed under different conditions. The measurements were carried out using a Philips PW1710 diffractometer (settings provided in Appendix A) and no gold coating of the samples was applied prior to measurements. Two patterns were collected at different spots of the surface of each sample. Averaging of the two patterns aided in removing casual errors in the measurements (e.g. accidental noise peaks or surface impurity influence) and the resulting spectra were further modified to remove any residues, i.e. accidental single-angle peaks mathematically equivalent to delta-functions. Also, the reliability of the XRD measurements was tested using the two repetitive runs: the corresponding measurement patterns showed only minor differences and it was found that the repeatability of the XRD results is sufficient.

The *acquired spectra were subsequently analyzed using Rietveld analysis*. The main difference of the Rietveld refinement as compared to conventional pattern treatments is the analysis of the entire spectra, not only the peaks in the pattern. In Rietveld analysis, single-number integrated intensities are replaced (i.e. spread out) by peaks of certain heights along the points, replacing measured singularities with smooth peaks. The method takes into account

overlapped data inclusive of a noise and background and is *more reliable than the method using the integrated intensities of overlapping peaks*. The mathematical apparatus of the procedure is given in Appendix A.

To perform a Rietveld analysis of the obtained XRD spectra of the samples, commercial TOPAS software (Bruker AXS, Inc., Madison, USA) was used. The standardized patterns for the particular phases were collected from ICSD databases (Inorganic Crystal Structure Database). To ensure uniformity and reliability of the results, *each pattern was processed using a standardized procedure* (Appendix A). Crushing and spiking of the coating samples using a standardized compound to determine the amorphous content was not performed.

The *Energy-Dispersive X-ray Spectroscopy* method was used to study the element composition of the produced samples and the initial powder feedstock.

The EDX measurements were carried out in the JEOL SEM 5600LV chamber with a 500x magnification under small working distances (less than 10 mm). The samples were gold coated (~ 14 nm thick layer) to facilitate easy orientation and proper system focusing. *A customized pattern for collecting the EDX spectra was constructed* (Appendix A) and five measurements per each sample were carried out to compensate any fluctuations.

During the subsequent spectra analysis, the gold detected due to the presence of the sputtered layer was removed and not included in the following weight balance calculations. Also, carbon atoms were not considered into the calculations and the measured peaks pertaining to C atoms were removed. As the EDX Si-Li detector was protected using a thin beryllium window, detection of hydrogen atoms (present in the HA structure) was not possible.

Based on the results provided by the software, *weight and atomic balances were calculated for every sample*. Additional experimental work on EDX reliability was carried out by multiple measurements of Ti-6Al-4V substrates spectra (Appendix A). It was found that the systematic calculation procedure is stable.

3.2.2.4 Porosity

As the *porosity* is one of the crucial factors influencing the process of acceptance of the implant in the patient's body (2.1.3), *several alternative methods were used* to measure this coating property [200-206].

Software analysis of the acquired coatings cross-sections micrographs was used to inspect the *internal porosity level of the produced coatings*. For this purpose, coating cross-section samples were prepared and processed as the samples for microstructure study (3.2.2.2). To avoid affecting the observations, the samples for porosity assessment were not gold sputtered.

Trial runs of the porosity analysis indicated that the images acquired by optical microscope are not suitable for the analysis due to partial blurring of the images caused by low depth of focus. It was shown that the influence of the blurring cannot be neglected and the measured values are deteriorated by this phenomenon. SEM images were therefore investigated as the acquired micrographs have sufficient depth of focus and high sharpness, important for successive detection of porosity edges. Secondary electrons mode was used for image capturing as this mode is more sensitive to the sample morphology.

To avoid loss of information, the images were acquired and processed in non-compressed format (".bmp" file extension) with dimensions of 640 x 480 pixels. To increase the results reliability, five images were captured at different points of every sample. To facilitate relative sample porosity comparison, all images were captured under identical SEM magnification. Low SEM magnifications allow sampling of larger cross-section area, increasing the statistical reliability. However, small pores and voids are omitted in the image analysis, influencing the calculated value significantly. Conversely, high magnifications exhibit fluctuations in measured values and standard deviations due to small sizes of investigated areas. Based on trial runs results, the 500x magnification was selected as optimal for the analysis. For this magnification, the dimensions of the image areas analyzed in the software were 256 x 192 μm . The analyzed areas of several samples were smaller due to inferior coating thickness.

Numerical determination of the internal porosity levels and an average pore size was subsequently carried out using software attached to the optical microscope (Image-pro plus, v3.0, Media Cybernetics, L.P.). The software allows *processing of the images acquired during microscopy and their graphic analysis*. The pores and voids in the acquired coating cross-section images exhibit different levels of digital contrast and brightness as compared to coating solid (splats). The different levels of brightness and contrast can be detected by the software using adjustable ranges. Based on trial runs, threshold detection levels for each of the ranges

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were selected prior to measurements. To ensure process uniformity, the threshold values were held at constant values during the entire analysis. As the brightness and contrast levels of the investigated images differed, different numbers of detection ranges were used for the subsequent software processing (2 - 4). The proper detection of the porosity in the images was monitored during the process: the edges of the detected porosity (pores, voids) were highlighted and confirming observations were carried out.

As the porosity assessed via the image analysis is computation-based, additional statistical processing was carried out to support the results credibility. The calculated sample porosities were mutually compared to find out whether the differences are statistically important. An F-test was performed to test the hypothesis that the standard deviations of two calculated sample porosities (considered as two normally distributed populations) are equal. With respect to the results provided by the F-test (equal or unequal standard deviations of the investigated samples), a t-test was subsequently performed to test the hypothesis that the mean averages of the two normally distributed populations are equal, i.e. the average values of the porosity levels of the two samples are equivalent. Both the F-test and t-test statistical method were carried out at 95% confidence levels.

Due to their extremely high density, this method *could not be used to assess the porosity of the cold spray coatings*. The thickness of the cold sprayed coatings was a limiting factor and the average pore size of the coatings was beyond the resolution of the used software at tested magnifications (< 2000x). Higher magnifications resulted in loss of image sharpness and could not be used for the analysis.

In spite of the efforts to retain the high level of the results reliability (SEM image acquisition, identical magnification, identical detection ranges, non-compressed image formatting, dual statistical testing), the internal porosity results provided by the image processing method are affected by the fact that three dimensional structure is evaluated using two dimensional images. The pores visible at sample cross-sections are two dimensional projections of three dimensional formations (spherical pores, irregular pores, voids). Simple geometrical visualization of an imaginary plane cutting a regular sphere indicates that the calculated porosity (the planar circle) will be different from the actual porosity (the three-

dimensional sphere) of the coating. The absolute values of the calculated internal porosity are therefore expected to be shifted systematically. However, the relative differences between the respective coatings will be retained.

Alternatively, the *coatings internal porosity was measured using a pycnometric method* (Accupyc 1330, Micromeritics Corp., Norcross, USA). The principle of the method consists in filling the calibrated hermetically sealed chamber volume with helium gas and measuring the volume of the sample within the chamber at a constant temperature (24.2 °C). Contrary to liquid penetration, the gas does not exhibit a surface tension and therefore even the smallest pores can be filled. As the gas penetrates through the connected sample voids and pores, the volume of the samples is determined exclusive of the open surface porosity. Subsequently, the density of the measured samples is calculated and the sample internal porosity is assessed by comparing with the bulk compound density (HA: Table 10, TiO₂: Table 12).

For the purposes, coatings of superior thickness were plasma sprayed (> 3 mm). The thickness of the coatings induced secondary stresses and a successive spontaneous coating delamination facilitated obtaining a free-standing sample coatings. The coatings were precisely weighted (Mettler Toledo balance, resolution 0.1 mg) and inserted into a standardized cylindrical Al crucible (19 x 39.8 mm, diameter x height, wall thickness 0.254 mm, weight 2.0951 g).

The reliability of the pycnometer device was tested (Appendix A) and credibility of the results was furthermore increased by performing multiple (3 by default) runs of the system for each sample. As the method requires thick free-standing coatings, the porosity of the cold sprayed samples could not be determined using this method.

To supplement the results obtained by pycnometric method, the *open porosity of the plasma sprayed samples was subsequently determined using a mercury intrusion porosimetry* (MIP). Analogous to helium pycnometric measurements, this method consists in filling the sample coating open porosity with liquid mercury and observing the changes due to the penetration of the liquid into the sample.

Mercury porosimetry is based on the capillary law governing liquid penetration into small pores. The mathematical model of the MIP could be found in Appendix A. The volume of

mercury penetrating the pores is measured directly as a function of the applied pressure. For the analysis, the sample is loaded into a penetrometer, a special glass container able to withstand the pressure load. The penetrometer is installed into a low pressure port. In the low pressure port, the penetrometer is evacuated and backfilled with mercury at various pressure levels up to 207 kPa. The data are collected at the selected pressure levels. The mercury filled penetrometer is then installed into a high pressure port. The high pressure analysis collects data at selected pressures up to 414 MPa.

To ensure mutual results comparability, the samples used in this method were the free-standing coatings previously used for the pycnometer analysis. The coatings porosity was determined and the respective average pores sizes were calculated. Specifications and settings of the mercury intrusion system, thermal calibrations of the porosimeters used and measurements of the system reliability are provided in Appendix A. The system exhibited a reduced consistency which had to be taken into subsequent considerations.

Additionally, the total (i.e. open surface and internal) coating porosity was determined from the fatigue lives experiments (3.2.3.1) and the software simulations (3.3.2) provided the internal coating porosity levels.

3.2.2.5 Surface Roughness

The *roughness of the coating surface* is another important factor in terms of the successful implant acceptance. A standardized procedure was used to measure several different roughness characteristics [207-209].

Surface roughness measuring system SurfTest SurfPak SV-614 (Mitutoyo Corp., Aurora, USA; Appendix A) was employed and SurfPak-SV software was used to measure five profile roughness indicators:

1. R_a , *mean deviation of the profile*: an arithmetical mean of the absolute values of the

profile deviations (y_i) from the mean line, $R_a = \frac{1}{n} \sum_i |y_i|$

2. R_q , *root-to-mean square deviation of the profile*: a square root of the arithmetical mean

of the squares of profile deviations (y_i) from the mean line, $R_q = \sqrt{\frac{1}{n} \sum_i y_i^2}$

3. R_p , maximum profile peak height: the maximum value of the profile deviations (y_i) from the mean line, $R_p = y_{\max}$
4. R_v , maximum profile valley depth: an absolute value of the minimum value of the profile deviations (y_i) from the mean line, $R_v = |y_{\min}|$
5. R_y , maximum height of the profile: the sum of height $y_{\max}$ of the highest point from the mean line and of depth $y_{\min}$ of the lowest point from the mean line, $R_y = y_{\max} - y_{\min}$

All five measured indicators are measured in micrometers and conform to ISO: 4287-1984 standard.

To reduce the influence of plasma gun spraying direction, the coated samples were measured in two perpendicular directions. Five samplings per each direction were recorded using a scanning speed of 1 mm s^{-1} . Four specimens were tested per each sample and an average value was reported as a measured coating quality.

Testing of *cold sprayed samples roughness* was performed with the same parameters. The roughness samplings were carried out only in one direction for cold spray samples.

Testing of the reliability of the surface roughness Surftest device (Appendix A) showed the relative magnitude of the deviations is negligible. The laboratory glass used in the reliability experiment was subsequently used as the substrates for cold spray experiments.

3.2.2.6 Adhesion Strength

Adhesion of a coating on a substrate is a parameter of utmost importance in hard-tissue replacement science. Attempts to achieve the highest possible coating adhesion among cementless implants led to the need to study this property in detail. In this study, *adhesion strength of the plasma sprayed coatings was studied according to ASTM-C633-01* “Adhesion of Cohesive Strength of Thermal Spray Coatings” standard [210-216].

The test specimens were Ti-6Al-4V cylindrical studs with a 25.4 mm diameter and cylinder height of 25.4 mm. The surface of the studs was roughened by grit blasting prior to the plasma deposition under standardized conditions (Appendix Table 13). The six coatings under selected PSP combinations were then deposited for both HA and TiO_2 powders, respectively. Twelve specimens were produced per each PSP set, all deposited en bloc to increase the results uniformity.

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The ASTM standard specifies the minimal coating thickness as 380 μm . As the coating adhesion is a function of the coating thickness (2.1.3), increased attention was paid to minimization of the influence of this factor: the number of plasma torch passes and the relative torch velocity during the spraying were selected based on the results of basic coating measurements (3.2.2.1) so as to produce coating samples of even thickness.

The coated cylindrical studs were then glued to identical, non-coated studs. The second set of studs was not grit blasted and the smooth stud surfaces were degreased and freed of oil using chemicals and subsequently dried. The selection of the bonding agent (glue) is prescribed by the ASTM standard: sufficient viscosity (to allow penetration of the glue to a certain depth into the coating) and adhesion strength higher than the highest coating adhesion strength is required.

FM 1000 adhesive film was selected as a suitable agent. FM 1000 (Cytec Engineered Materials, Inc., Havre de Grace, USA) is a modified polyamide-epoxy unsupported adhesive film developed for high-strength bonding applications, tested against the requirements of MMM-A-132 specification (U.S. Federal standard, class 1). The standard tensile strength of the agent is 24.82 MPa, as provided by the manufacturer.

A hot press device was used for curing the bonding film. However, the typical cure for the FM 1000 bonding agent (pressure of 0.28 MPa at 170 °C for 60 minutes) was not followed. Trial runs of the experiments showed the curing of the bonding agent was not satisfactory and debonding of the FM 1000 film was often observed during the subsequent pull-out testing. Different curing parameters were used instead: the used pressure was 7.31 MPa and the curing period was extended to 180 minutes. As the temperature of the hot press blocks and the bonding agent differ, the temperature of the bonding agent was monitored in-situ using a digital thermometer (Tecpel 305 A-1, resolution 0.1 °C, accuracy ± 0.3 °C). The average temperature of the bonding agent during the curing process was measured as 190 ± 0.3 °C. All 12 specimens were cured at the same time to increase results uniformity. Soft aluminum sheets were mounted onto both the upper and lower block of the hot press to ensure uniform pressure over the 12 specimens.

The cured samples were then ruptured using Instron 5569 static tester pull-out device. The increasing tensile load was applied at a low constant rate of the cross-head specified in the ASTM standard, 0.013 mms^{-1} . The experiments were carried out at ambient conditions (24 °C, air humidity 80%). The specimens which broke in unusual way were omitted from the average value computations.

The samples deposited using the cold spray technique are expected to give rise to higher levels of coating adhesion (2.1.3). However, insufficient thickness of these coatings invalidated the adhesion strength testing.

The reliability of the test specimen production process was tested (Appendix A). The results show that the variations of the results are not negligible and the sample preparation process does have an influence on the measured values.

3.2.2.7 Micro-hardness and Elastic Modulus

Additionally, *micro-hardness of the produced coating samples was tested*. The testing provided information on the *coating hardness and elastic modulus*, a material property important for coating adhesion due to a presence of internal stresses [195,217,218].

The micro-hardness was tested using MTS NanoIndenter XP (MTS Nano Instruments, Oak Ridge, USA) equipped with Nano-CSM continuous stiffness measurement unit for dynamic characterization of surfaces, interfaces and thin films (specifications at Appendix A).

The tested specimen is mounted on a precision controlled x-y stage for positioning of indents. Force and displacement versus time are recorded during the cycle of indentation from which the material hardness and elastic modulus can be calculated.

Initially, the specimens intended for the micro-hardness measurements were sample cross-sections prepared using a standardized procedure described in 3.2.2.2. However, the indentation points could not be specified accurately for the thin coatings due to limitations in the used device. This resulted in occasional partial indentations into the surrounding resin or the Ti-6Al-4V substrate. Result of such indentation would then significantly alter the measured average values of the coating micro-hardness and elastic modulus. Instead, indentation into the samples was carried out in a direction perpendicular to the coating surface. This procedure ensured successful indentation into the coating. However, contrary to the polished cross-

section samples, the measured values could be affected by the coating surface roughness. The influence of the coating roughness on the measured values was not assessed.

Five loading and unloading cycles (sample unloaded to 90% of the current load) with increasing load were made during one indentation. Each cycle provided one data point of material stiffness, elastic modulus and micro-hardness. The data points under the last loading cycle were included in the average value calculations. Ten indentations per sample were made using the Vickers indenter geometry with the maximum loading force of 10 gf. Values from invalid measurements were omitted from the subsequent calculations. The system parameters used are given in detail in Appendix A.

Reliability measurements of the device (Appendix A) indicated the repeatability of the measurements is high.

3.2.3 Complementary Measurements

Complementary measurements were carried out to extend the scope of the work and to provide a different insight on the plasma spray process.

3.2.3.1 Fatigue Life Experiments

The variety of the coated implants applications brings along the problems of designing implants able to withstand mechanical loads of various nature. One of the important factors influencing the performance of the implant is its *ability to resist cyclical mechanical loading* arising during its usage in patient's body. An experimental program assessed *fatigue properties of plasma sprayed specimens* prepared under different PSP: the influence of the coatings on the fatigue lives of the deposited specimens was studied [142,219-221]. In case of ceramic coatings (HA, TiO₂), the arising internal stresses operate as barriers for cracks initiation and the first stage of propagation, increasing the fatigue lives of specimens, as given in detail in 2.1.3.

The coated samples were prepared under three different PSP sets for both HA and TiO₂ powders (Table 22). The sets were denoted as HA-1 to HA-3 and TiO₂-1 to TiO₂-3. A constant feedrate was used for production of all the sets. However, due to different deposition efficiencies of spraying of both powders, different system RPM were used for different powders: 8 for HA and 3 for TiO₂ powders, respectively.

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Table 22: PSP sets for production of fatigue experiments samples

Fatigue experiments set	Net power [kW]	Main gas flow [scfh]	Auxiliary gas flow [scfh]	Carrier gas flow [scfh]	Hopper revolutions [1]	Spray distance [mm]
1	15	100	80	15	8, 3	120
2	12	80	60	15	8, 3	140
3	10	60	40	15	8, 3	160

To expand the knowledge of the influence of the deposited coatings on the fatigue lives of the specimens, in-flight properties of both powders were measured for each of the selected spraying sets. (SprayWatch settings for this measurement could be seen from Table 14). The average values of temperature and velocity of the particles could be seen from Table 23.

Table 23: In-flight powder properties of fatigue lives experimental sets

Fatigue experiments set	Temperature [K]	Velocity [ms ⁻¹]
HA-1	2352 ± 9	199 ± 3
HA-2	2160 ± 34	150 ± 2
HA-3	1778 ± 57	132 ± 4
TiO ₂ -1	2385 ± 15	197 ± 2
TiO ₂ -2	2267 ± 16	167 ± 2
TiO ₂ -3	2168 ± 37	128 ± 2

As the device for the fatigue lives testing requires a complex designing of the substrates, the specimens were custom-made using CNC tools. Geometric specifications of the substrates could be seen from Fig. 3-3 as well as examples of typical as-fabricated, grit-blasted and coated specimens. Longitudinal symmetrical design of specimens enabled carrying out two fatigue measurements for one sample, increasing the total number of measured data.

Due to the extensive usage of material (substrate thickness 4 mm) and the requirements for precise sample machining, low carbon steel (class 11) was used as a substrate. To remove the oxide layer from specimens surfaces and ensure better coating adhesion, grit blasting of specimens was carried out following a standard procedure (Appendix Table 13). Surface roughness measurement indicated values of $R_a = 4.972 \pm 0.773 \mu\text{m}$ and $R_q = 6.330 \pm 0.887 \mu\text{m}$.

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Fig. 3-3: Specimens for fatigue lives experiments: a) specimen geometry, b) as-fabricated and grit-blasted specimen, c) coated specimen

A special procedure was used to control the robotic arm to ensure coverage of the entire specimen and even coating thickness (the coating thickness influences the magnitude of the internal stresses and therefore the fatigue lives of the sprayed specimens). The results of the thickness per torch pass measurements (3.2.2.1) were used in sample preparation. Both sides of all specimens were coated with the target thickness of each coated side set to $\sim 400 \mu\text{m}$.

For both powders, five specimens were prepared for each set. The thicknesses of both sides of coatings on all specimens were measured at five different specimen locations. The average measured coating thicknesses could be seen from Table 24.

As could be seen, the final thicknesses of the produced HA coatings varied. The variations in coating thicknesses within respective sets were caused by functional limitations of the plasma system during the spraying period due to the impossibility to spray the specimens in a single batch. The thicknesses of the produced TiO_2 coatings produced latterly were uniform and matched the target thickness well.

Table 24: Coating thicknesses of fatigue lives experimental specimens

Specimen	Coating thickness [μm] (side A/side B)											
	HA-1		HA-2		HA-3		TiO ₂ -1		TiO ₂ -2		TiO ₂ -3	
1	540	908	300	378	368	754	392	404	394	392	406	380
2	682	588	282	298	754	232	394	400	392	402	394	378
3	660	1444	552	152	662	402	388	396	396	402	392	376
4	508	994	272	386	1088	384	402	402	408	390	390	394
5	546	394	326	378	406	380	402	404	404	396	388	390

Another set of grit blasted specimens was not subjected to the coating deposition process. This reference set of specimens was subjected to fatigue lives experiments and used for comparison purposes.

The fatigue tests were carried out using an electromagnetic computer controlled SF-Test device (Department of Materials, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University). One end of the flat specimens was clamped in the SF-Test anchorage while the other end was equipped with a ferromagnetic yoke and deflected by an alternating electromagnetic field. The specimens were subjected to a symmetrical cyclical bending load (as cantilever beam) with constant deflection of the free end at room temperature. The loading frequency corresponded to the first natural frequency of the mounted specimens (usually between 70 – 100 Hz) and was maintained using phase locked loop technique. As utilization of the resonance effect was chosen to achieve the required deflection amplitude, the loading frequency was kept close to the actual resonance frequency of the specimen - yoke system. A feedback regulation altered the loading frequency so that the deflection amplitude of the free end of the specimen remained constant.

The changes in the resonance frequency of the specimen - yoke system and, subsequently, the changes in the loading frequency depend on the fatigue crack area. Therefore it is possible to estimate specimen cross-section damage from the changes in the loading frequency. Based on previous results, a frequency drop of 4 Hz was chosen as a fatigue test stopping condition. At such drop the fatigue life is represented by the number of loading cycles and corresponds to approximately 40% damage of the specimen's cross section.

The data obtained from the experiments were re-calculated using standardized mathematical procedure. Weibull plot of data was constructed to find out respective series influence on specimens fatigue lives. Numerically, the influence of the plasma spray surface treatment on the fatigue life could be characterized by the relative fatigue life R_f , defined as the proportion of the mean fatigue life of the set with given surface treatment to the mean fatigue life of the reference set (i.e., $R_f = 1$ corresponds to the relative fatigue life of reference specimens).

Additional computations were performed using the fatigue lives experimental results. Assuming identical geometry, density and Young's modulus of the substrates prior and after the deposition process and homogeneity, isotropy and linear elasticity of the coating material, *Young's modulus, density and porosity of the coatings could be calculated.*

Using linear elastic finite element method (FEM) simulations of a specimen under bending load, it was found the computed resonance frequency resembles a behavior of a single degree of freedom oscillator following the momentum equation:

$$M_{\text{applied}} = E_s w \int_0^{\frac{H}{2}} \frac{d\varepsilon}{dx} x^2 dx + E_c w \int_{\frac{H}{2}}^{\frac{H}{2}+h} \frac{d\varepsilon}{dx} x^2 dx \quad \text{Eq. 8}$$

where E_s , E_c are the substrate and coating moduli, respectively, H is the thickness of the substrate (4 mm), h is the coating thickness and w is the deflection at given distance x .

The measured resonance frequency of real specimens as well as geometrical measurement of coating thicknesses and weights of substrates and coatings allowed calculating of the coatings moduli and density. Using the calculated and bulk material density, the coating overall porosity (i.e. internal + open) was calculated.

Fatigue properties of the sprayed bodies are microstructure dependent. As the microstructure of the specimens cannot be controlled, the final fatigue properties are partly stochastic. Some variations were therefore expected in the results.

3.2.3.2 Single Splats Collection

As given in detail in section 2.1.1.2, the final *coating characteristics are highly influenced by the formation, shape, morphology and spreading behavior of the solidifying*

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splats. This influence is particularly accentuated in the case of the first deposited layer, i.e. the initial contact between the substrate and the sprayed material.

An *additional experimental work* was carried out within this study: mirror-polished substrates were prepared and individual splats were deposited via prepared shutter apparatus. Six sets of splats were collected (denoted as SS-A to SS-F) for each of the powders according to the six previously selected sets of PSP (3.2.2). *Geometric splat properties (morphology, shape, eventual splashing) were studied* using optical and SEM microscopy.

To retain mutual comparability with the sprayed coatings, Ti-6Al-4V substrates were used for the single splats collection. The x-y dimensions of the substrates were measured as 29.08 x 24.11 mm. Trial runs of the experiments showed the dimensions of the samples were sufficient to comprise the entire cross-section of the plasma jet at respective distances, allowing studying the differences between the splats deposited in the middle of the jet and within its peripheral areas. The substrates were ground and polished following a well-established procedure (3.2.2.2). To achieve excellent surface smoothness, a 1 μm diamond paste was used additionally. The roughness of the polished substrates was measured as $R_a = 0.047 \pm 0.007 \mu\text{m}$ and $R_q = 0.067 \pm 0.007 \mu\text{m}$, i.e. comparable to the laboratory glass surface measured in section 3.2.2.5. The polished substrates could be seen from Fig. 3-4.

Fig. 3-4: Mirror polished substrates for single splats collection

Contrary to the grit-blasted substrates used for coating depositions, the polishing procedure was carried out to facilitate easier splat morphology observations and to reduce the influence of the substrate roughness as one of the factors influencing the results. As this mechanical interlocking factor was eliminated, the final splat characteristics were mostly influenced by the studied in-flight particle properties. The mutual difference in the roughness of the grit-blasted and polished samples is expected to give rise to a different spreading behavior of the splats and it is necessary to take this difference into the consideration in the evaluation phase.

As the number of deposited splats is too high during one pass of the gun, it was necessary to reduce the number of particles impinging the substrates. Trial runs using increased robotic arm translational speed were not effective until reaching high velocities. Such velocities would, however, influence the solidification behavior of the droplets and the resultant shape of the splats would differ from the shape of splats deposited during other experimental work. To decrease the number of deposited splats and maintain the spraying conditions equivalent to the other spraying experiments, a special shutter apparatus was constructed. The shutter was placed in the vicinity of the prepared substrate holder, shielding the substrate from the plasma jet. The plasma was started and the powder was fed into the jet. The shutter was then opened for a short period of time (~ 0.5 s) to facilitate collection of the splats and closed again.

The substrate prior to the splats collection was held at ambient temperature, i.e. below the transient temperature described in 2.1.1.2. Splashing or partial splashing of the impinging droplets could therefore be expected. Recrystallization and phase changes of the material within the splats were not examined in this study.

3.2.3.3 Subsidiary measurements

Two additional experimental methods were used in this study. Analysis of particle size distributions of the powders was carried out using a precisely calibrated laser device and surface roughness and density of the Ti-6Al-4V substrates prior to the deposition of the coatings were assessed.

The *particle size analysis of both powders* was carried out using a Fritsch Analysette 22 NanoTec device. The device uses two vertically aligned semiconductor lasers (wavelength 655 nm, safety class 3B) to illuminate a cell containing a liquid suspension of the measured

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powder. The convergent laser beam is scattered on the powder particles when passing the measuring cell and the scattered intensities are detected by a multi-element detector array with 80 individual elements. As the scattering angle is related to the diameter of the particle causing the scattering, the particle size distribution can be subsequently calculated using complex mathematics (Fraunhofer-Mia theory). Basic specifications of the Analysette 22 device could be seen in Appendix A.

Prior to all measurements, the liquid suspension cell and the circulation system of the NanoTec device were disassembled and cleaned thoroughly using acetone. The device was calibrated using a Fritsch F-500 standard sample.

The detection range of the device is directly related to the laser work distance. As the laser working distance was set to 72 mm for all successive measurements, the detection range was 1.39 - 191.17 μm , spanning the entire particle size ranges of both used powders. This detection range was extended for the measurement of SiC powder (particle sizes up to 850 μm) used for grit-blasting of the substrates prior to spraying (Appendix A).

For the measurements, two different dilutions were prepared for each powder - 9% and 15%. Five measurements were carried out for each dilution and the average and cumulative powder particles size distribution factors were recorded.

The reliability measurements of the particle size analyzer device showed the size distribution measurements are consistent (Appendix A).

Supplemental measurements were carried out in order to assess the properties of the Ti-6Al-4V substrates used in the study. Some properties of the used alloy were measured as an integral part of the reliability testing of other devices (phase composition, porosity, micro-hardness). *Additionally, roughness and density of the substrates were measured.* As both the quantities are substrate-only dependent, the results will be provided in this section to maintain easy orientation in the results chapter.

The Ti-6Al-4V substrates used for both PS and CS experiments spraying were grit-blasted following the procedure described in 3.2.2. The 45° grit-blasting angle could have affected roughness differently in different directions. To eliminate the influence of the grit-blasting

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angle and unify the results, the roughness was measured in four perpendicular directions and average values per each direction were calculated.

Table 25 shows the measured average values with respective standard deviations. According to the roughness reliability testing, the roughness values correspond approximately to the #1000 SiC sand paper.

Table 25: Roughness of Ti-6Al-4V substrates prior to coating deposition

Measured roughness parameter	Value [μm]	
	Average	Standard deviation
R _a	5.074	0.320
R _q	6.470	0.428
R _p	18.142	1.605
R _v	18.632	1.227
R _y	36.775	2.727

Another important property of the substrate is the density and, subsequently, elastic modulus and hardness. As the literature indicates different values of the density of Ti-6Al-4V alloy (generally 4.43 - 4.50 gcm⁻³), it was decided to conduct an auxiliary measurement.

Using a densimetric method, four Ti-6Al-4V samples of different weights were weighed three times in air. Subsequently, they were immersed in a commercially available ethanol of the known density (Sino Chemical, T ETH-019, $\rho_{28^{\circ}\text{C}} = 0.7890 \text{ gcm}^{-3}$) and weighed three times again. The density of the substrates could then be calculated from

$$\rho_{\text{Ti6Al4V}} = \frac{m_a}{m_a - m_e} \rho_e \tag{Eq. 9}$$

where m_a , m_e are the sample's average weights in air and ethanol, respectively and ρ_e is the density of the ethanol used. To increase the reliability of the measurement, the same samples were dried and the experiment was repeated using 2-propanol (Rieden-de Haën, 40219 Puranal, $\rho_{28^{\circ}\text{C}} = 0.7860 \text{ gcm}^{-3}$).

The density of the Ti-6Al-4V substrate measured using the densimetric method was calculated as an average value of the measurements in both ethanol and 2-propanol. The value $\rho_{\text{Ti6Al4V}} = 4.4179 \pm 0.0087 \text{ gcm}^{-3}$ is lower than indicated in the literature. However, the standard deviation of the measured density is low and the result could therefore be assumed accurate.

The value also fully corresponds to the density measured using pycnometric method (3.2.2.4).

3.3 Software Simulations

To further extend the experimental work carried out within this study, *various software simulations were performed*. The in-flight particle properties measured in 3.2.1 were simulated as well as the selected final coating characteristics experimentally assessed in 3.2.2. Complementary simulations were also performed to supplement the results of the powder feedstock XRD measurements as well as prediction of the spreading behavior and solidification of single splats, experimentally carried out in 3.2.3.2.

3.3.1 *Particles In-flight Properties Simulations*

The first part of the experimental work addressed the measurements of the *powder in-flight properties* (the temperature and the velocity of the particles). As such properties greatly affect the final coating characteristics, numerical simulations were performed to assess this phenomenon.

Two different software codes were used: TrajMet software for computation of the trajectory, temperature and velocity of metallic or ceramic particles injected into a two-dimensional plasma jet flowing in the air at atmospheric pressure. The TrajMet software could be optimized to use the results of the Jet de Flow software to compute the properties of the plasma jet. However, it was discovered the functionality of the code is limited and the results are unreliable. It was therefore decided not to involve the software into discussion.

Jets&Poudres software assistant (SPCTS, Université de Limoges, France) for computation of the thermal and motion behavior of the particle inserted in different points of the plasma jet was used. In the first stage, Jets&Poudres collects data necessary for the plasma jet generation. The default values used in the Jets&Poudres software were updated to match the NTU plasma system specifications. A summary of the crucial characteristics could be seen from Table 26.

The net power parameter, thoroughly studied according to OAAT and the Taguchi designs is integrated into the software using gun electric power and efficiency ratio. The value of the gun electric power was calculated to match the desired net power. The flow of the gases was a limiting factor due to impossibility to select any arbitrary Ar/He ratio. Only three combinations of the gas flows are provided in the software: 100% Ar 0% He, 70% Ar 30% He and 0% Ar

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100% He. As the combinations used in both the designs correspond predominantly to the 70% Ar 30% He ratio, this combination was used for all calculations.

Table 26: Software settings for the plasma jet generation simulations

Jets&Poudres plasma generation parameters	Value
Plasma gun inner diameter	8 mm
Gun electric power	10 - 30 kW
Gun efficiency	30 - 70%
Total gas flow	30 - 90 lmin ⁻¹
Upstream flow pressure	100 kPa
Surrounding atmosphere	air
Initial min. axis temperature	12000 K
Spray distance	50 - 150 mm

The position of the powder injector could be altered in the software. However, the allowed position of the injector is a non-negative value with respect to the gun, i.e. the software only simulates external powder feeding. This is different to the SG-100 internal injection.

In the second stage, a single powder particle is virtually inserted into the plasma jet distribution field calculated in the previous stage (Fig. 3-5).

Fig. 3-5: Particle trajectory and temperature changes in Jets&Poudres software

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It was discovered *the input values of the powder properties* have a vital impact on the final calculated properties and cautious selection is therefore necessary. The values of the powder properties used in current simulations (also used for other software simulations) could be seen from Table 27, as extracted from the literature and/or respective measurements.

Table 27: Properties of the HA and TiO₂ powders used in software simulations

Selected powder property	Unit	HA	TiO ₂
Mass density (solid / liquid)	gcm ⁻³	2.904 / 3.210	3.671 / 4.274
Particle diameter	μm	39.90	32.20
Particle initial temperature	K	300	300
Melting point	K	1943	2113
Boiling point	K	3500	3020
Thermal conductivity (solid / liquid)	Wm ⁻¹ K ⁻¹	1.867 / 2.2589	12.5 / 3.34
Specific heat (solid / liquid)	Jkg ⁻¹ K ⁻¹	730 / 1347	710.6 / 1421
Latent heat (melting / boiling)	kJkg ⁻¹ K ⁻¹	15.4 / 456.1	875 / 5750
Viscosity	m ² s ⁻¹	2.1 x 10 ⁻⁶	1.6 x 10 ⁻⁶
Surface tension	Nm ⁻¹	0.476	0.445

As the boiling point of TiO₂ is ambiguously indicated as 2770 – 3270 K in the literature, an average value of 3020 K was used. The density of the powders in a solid state was measured using the reliable pycnometric method and differs slightly from the literature.

In the third, last stage, the temperature and velocity of the particle inserted into the simulated plasma jet was read at different distances from the plasma torch. The readings provided a unique alternative to the measured results. Due to the difference in the powder feeding and the impossibility to select exact Ar/He gases ratio some deviations in the results were expected as compared to the experimentally measured values.

3.3.2 Coating Characteristics Prediction

The experimental work carried out within this study provided information on the selected properties of the final deposited coatings. Additionally, some *properties of the coatings were evaluated using software simulations*.

Simulent Coat software code (Simulent, Inc., Toronto, Canada) was used to simulate the coating deposition process. Simulent Coat is a three dimensional stochastic model of thermal spray coating production process using Monte Carlo technique to determine the random droplet

impact capable of predicting the *coating porosity, thickness and roughness*, and the variation these properties with the input spray parameters.

It was decided to simulate the six selected combinations (PS-A to PS-F) according to the Taguchi method for both powders. The simulations were carried out in four stages:

In the first stage, the calculation domain parameters are provided. A default size of 50 x 1000 μm of the computational domain was used for the calculations. The number of grids in the mesh (16 x 301; analogical to FEM meshing) was selected so that the number of grids was identical in both directions.

In the second stage, the data of the particles in-flight properties were entered. The values of the temperature and velocity and their respective standard deviations were acquired from the experimental results according to the Taguchi design (5.2) and the values of mean particle sizes and the respective standard deviations were acquired from the results of the laser particle size measurements (4.2.2.4). Influence of the random seed generator number (a number used for generation of random numbers, analogy of various stochastic influences in coating build-up) was tested (Appendix A). A value of 235 was used for all calculations.

In the third stage, the powder feeding parameters were inserted as well as the parameters of the robotic arm movement during the process. In order to accurately follow the real experimental work, the powder feeding parameters were selected according to the RPM conversion experiment carried out in Appendix A. The velocity of the robotic arm was selected according to the real spraying parameter (Appendix Table 14), i.e. 100 mms^{-1} for both powders. The spray distance parameter was selected as required by the respective spraying combination. Initially, the number of passes parameter was selected as 15 and 10 for HA and TiO_2 , respectively (Appendix Table 14). However, it was discovered the software cannot compute higher number of passes for some combinations, particularly the combinations with relatively high feedrate. The number of passes was therefore reduced to 2 and the thickness was recalculated per one pass. As this change in the procedure could influence the results, a stability test of results after different number of passes was carried out (Appendix A).

In the fourth stage, the properties of the material were provided. The values used were acquired from literature and respective measurement and are summarized in Table 27. As the

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substrate was not pre-heated prior to the deposition process, an ambient temperature was used in the calculations.

Based on the parameters provided, the software calculated the final coating properties (porosity, roughness and thickness, Fig. 3-6) and the values were used for comparison purposes with the real experiments.

Fig. 3-6: As-deposited coating and its properties in Simulent Coat software

The reliability of the software was tested (Appendix A).

3.3.3 Complementary Computations

3.3.3.1 Powder XRD pattern predictions

A significant part of the study is the measurement of the relative differences in the phase composition of the coatings sprayed under different PSP sets (3.2.2.3) and the changes as compared to the original powder feedstock. However, the produced HA and purchased TiO_2 powders cannot be considered pure materials (i.e. single-phase compounds) as the presence of impurities and other phases is to be expected. The additional phases and/or impurities could be detected by the Rietveld analysis of the powder XRD patterns. To aid the detection, a *computer simulation was performed to obtain a single-phase material pattern prediction.*

The prediction of the XRD pattern of the two powders was carried out in two steps. Initially, the ICSD standardized patterns used in Rietveld (#26205 for HA, #23697 for TiO_2) were used in ATOMS software (Shape Software, Kingsport, USA) to obtain geometrical features of the respective compound (symmetry, space group, hkl planes, d spacing, etc.). Subsequently, the calculated geometry was used in PowderCell software (Federal Institute for

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Materials Research and Testing, Berlin, Germany). PowderCell is a program for the manipulation of crystal structures and for the calculation of the corresponding X-ray (or neutron) powder pattern (Fig. 3-7).

The computed XRD pattern prediction was based on the information provided by ATOMS program. Pseudo-Voigt profile function was used for the prediction of the pattern. The calculation range was set to $2\theta = 20 - 70^\circ$ with 0.01° step to match the real measurement range. Single wavelength radiation source was used and preferred orientation of the crystalline structure was not used. The predicted XRD pattern was compared to the as-measured patterns of the powders (4.2.2.1).

Fig. 3-7: Powder XRD pattern prediction in PowderCell software

3.3.3.2 Single Splats Solidification Simulations

Final part of the *software simulations addressed the phenomenon of single splats solidification and spreading*, experimentally carried out following a procedure described in 3.2.3.2.

For this purpose, Simulent Drop software (Simulent, Inc., Toronto, Canada) was used. Simulent Drop is a Volume of Fluid (VOF) free surface based code which allows simulations

of single (or multiple) droplet dynamics with phase change. Based on simultaneous calculation of momentum and energy equations, it uses advancing or receding contact angles during the impact on various surfaces. The simulation proceeds in several steps, in which various parameters were entered:

The time step for the calculations was selected as $\Delta t = 0.001 \mu\text{s}$ to involve smallest changes in the splat behavior and the total simulation time was set to $t = 5.000 \mu\text{s}$ to include the entire solidification process of the impacting splat. Ambient temperature prior to deposition (25°C) and zero roughness of the substrate was considered, with perpendicular orientation to the velocity vector of the incoming droplet. A data file with the Ti-6Al-4V substrate material properties was compiled according to the measured data and data from literature.

Secondly, the parameters of the incoming droplets were entered. The material thermal properties and particle size values used for the computations can be seen from Table 27. Initial droplet velocity and temperatures were selected according to the measured data of the six selected combinations in the Taguchi design (5.2). As the impact velocity of the droplets is relatively high, a static contact angle (90°) was used in the computations.

Symmetric boundary conditions of the impact were used in the third step of the process, i.e. only $\frac{1}{4}$ of the droplet impact geometry was simulated. The resulting shape of the solidified particle was calculated using mirror-conditions along two symmetry planes. The thermal boundary conditions were set to adiabatic along both symmetry planes and at all edges except the plane of the contact between the droplet and substrate where the 'known initial temperature' condition was used.

The computational domain of $140 \times 140 \times 70 \mu\text{m}$ was divided into a $104 \times 104 \times 52$ grid. The size of the computational domain was based on trial computations to ensure sufficient area to cover the prospective splashing and the grid was selected to provide high spatial resolution for detail analysis of the final splat shape.

Post-processing and plotting of the calculated results was carried out in TecPlot software (TecPlot, Inc., Bellevue, USA), a software for three-dimensional visualization of data. The resulting shape and morphology of the simulated solidified particles provided an alternative view on the experimental work carried out to capture single splats.

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The disadvantage of the simulation method using Simulent Drop software is the impossibility to simulate partially molten particle prior to impact. The particle material is assumed completely molten, a condition which is not necessary satisfied, particularly in the case of bigger particles where the core of the particle remains solid even when the surface is molten (Fig. 2-1). As the software does not allow solid state particle simulations, the influence of this limitation could not be tested.

Additional observation was made during the computations. The substrate temperature was monitored during the simulation and it was found that the temperature remained below the melting point of the Ti-6Al-4V alloy for all simulations. The *melting of the substrate should therefore not occur*.

CHAPTER 4: POWDER FEEDSTOCK

This first part of this chapter provides information on the *powder feedstock* used for the experimental work carried out within the study: *in-house produced HA* and *commercially available TiO₂*. In the second part, processing of both powders is described as well as characterization techniques employed to assess their properties.

4.1 Used powders

As described in the biomaterials section (2.2.2), the *traditional HA powder* is still the most widely recognized hard-tissue implant material due to its favorable biocompatible properties and close resemblance to human bone. Also, the pioneer research of the potential of the *novel TiO₂ material* suggests high biocompatibility of this compound. Mutual comparison of the traditional HA and novel TiO₂ powders in the process of thermal deposition would provide another information to the investigated mosaic.

4.1.1 *Hydroxyapatite*

The general properties of hydroxyapatite were provided in section 2.2.2.2. For the plasma and cold spray deposition techniques, it was necessary to use a *powder suitable for the process*, i.e. with good flowability, little or no impurities and acceptable particle size.

Initially, two commercially available HA powders were available for the experimental work. Both the powders were characterized using XRD, SEM, EDX and particle size analysis techniques. However, it was found that the quality of the powders is inapplicable for the experiments due to an insufficient flowability and impurities contamination. Due to the limitations, *it was decided to use an in-house produced HA powder*. The properties and characteristics of the produced powder can vary significantly and it was therefore *necessary to control the properties of the produced powder*.

4.1.1.1 Hydroxyapatite Powder production

Hydroxyapatite powders can be synthesized via numerous production routes, using a range of different reactants: sol-gel methods, hydrolysis of other calcium phosphates or hydrothermal techniques, e.g. reacting a mixture of calcium carbonate (CaCO₃) and di-ammonium hydrogen phosphate ((NH₄)₂HPO₄) at high temperatures and pressures. The most

popular methods for producing hydroxyapatite powders are *precipitation techniques*. Two precipitation reactions are commonly used:

Eq. 10

Eq. 11

The former precipitation method generally results in a faster production rate, with ammonium hydroxide being added to maintain a constant pH. However, this approach requires washing of the precipitate to remove harmful nitrates and ammonium hydroxide and the total effectiveness of the process is deteriorated.

The latter precipitation method, also referred as *wet chemical synthesis method* is slower, however, the only by-product of this reaction is pure water and also the method can be easily monitored and controlled. It was therefore decided to use this method for the production of the HA powder [62,222].

Using the method, 8 liters of orthophosphoric acid water solution (553.4 g of acid in the solution) was added under controlled rate into 8 liters of dilute solution of calcium hydroxide (592.8 g of hydroxide in the solution). Thorough stirring was maintained throughout the process and the resulting slurry was held at constant temperature.

Three different calcium hydroxides were tested for the production. However, the production process was found to be non-optimal for two of them and Rectapur $\text{Ca}(\text{OH})_2$ (Sino Chemical Pte., Singapore, purity > 96%) was therefore used. The orthophosphoric acid was 85% dilution (Merck, Pte. Ltd., Singapore).

As for many other precipitation methods, the crystallinity and purity of the products depend strongly on the preparation conditions [223]. A precise *control of the process parameters* (particularly solution pH and temperature) was therefore of utmost importance.

The higher the *processing temperature*, the higher is the *crystallinity* of the produced HA. For this process, the selected constant temperature was 36.8 °C. Initially, the *pH* of the $\text{Ca}(\text{OH})_2$ solution was ~ 12. As the acid was added in a dropwise manner, the pH of the solution decreased and the process was terminated when the pH value dropped below 9

(solubility and stability of calcium phosphates changes with pH, as given in Fig. 2-22). Expected yield for this process was ~ 800 g of HA powder per batch (prior to sieving).

In order to precisely monitor the pH of the aqueous solution, the pH meter (PH210, Hanna Instruments, Ltd., Great Britain) was calibrated using three pH buffers (4, 7 and 10).

It was then necessary to remove the water from the produced slurry and produce a powder of suitable particle sizes. Three different methods of different efficiencies were tested:

Furnace drying of the powder was carried out. The temperature was set to 400 °C and the slurry was dried for 60 min. The resulting substance was then ball-milled (Planetary ball-mill Pulverisette 5, ZrO₂ grinding medium; 100 RPM, 120 min).

Filtration of the slurry via filter paper was followed by additional furnace drying (300 °C for less than 60 min), followed by identical ball-milling procedure.

The efficiency of the two processes was, however, inferior and the yield was low. Furthermore, the produced powder particle size range was broad, making the powder unsuitable for both plasma and cold spraying.

A third powder *production method using a spray drier device* (Ohkawara Kahkoki, Co., Ltd., Yokohama, Japan) was therefore selected. Atomization process in the spray drier, i.e. simultaneous separation of the slurry into droplets and drying the droplets into fine particles, can be carried out using two different extensions of the device: a *rotary atomizer* or spray nozzle atomizer. Trial experiments showed the spray nozzle atomizer is not suitable for the HA powder production process as the dried slurry blocked the inlet hoses and the atomization nozzle frequently (installation and subsequent intake of the slurry through a fine sieve did not improve the situation significantly). The rotary atomizer proved to be the most efficient method for the HA powder production and the HA powder used in all the experiments within this study was prepared using this method.

As the main *aim of the HA powder production process was to obtain a powder of high crystallinity, high purity and desired particle sizes* (i.e. suitable average size and narrow size range), while, at the same time, retain high production yield, an auxiliary experimental work was carried out.

Trial experimental runs showed the resulting powder properties are influenced by three dominant factors: the flow of the slurry into the atomizer, the atomizer frequency (i.e. atomizer disc revolutions) and the temperature inside the drying chamber. As the optimal values of the three factors were found to be correlated, a number of possible combinations were tested. For each combination, the slurry was atomized for 30 minutes and the powder properties were evaluated using particle size analysis and SEM observations. The total process yield was monitored using weighing method.

The flow of the slurry is influenced by the settings of a rotary pump feeding the slurry into the atomizer. As the initial indication of the flow in the hose is in impracticable units (% of pump revolutions), a conversion experiment was carried out. For selected values of the pump revolutions (min. 10%, max. 50%, 5% increment step), the slurry was collected for three minutes and weighed every minute. An average flow (in gmin^{-1}) was then calculated as an average value of the three measurements. It was found that the lower flows ($< 30 \text{ gmin}^{-1}$) resulted in a production of fine particles ($< 20 \mu\text{m}$). Such particles are unsuitable for the high temperature plasma spray due to prospective extensive evaporation of the fine particles. High slurry flows ($> 160 \text{ gmin}^{-1}$) resulted in insufficient slurry drying and quality deterioration even at elevated chamber temperatures. Additionally, this measurement allowed determining the average density of the produced HA slurry as $\sim 1.0434 \text{ gcm}^{-3}$.

The atomizer frequency and linked revolution of its disc were found to be the crucial factor for the HA powder production. Two atomizer frequencies were tested (10 and 35 Hz), corresponding to approximately 4,170 and 14,580 revolutions per minute, respectively.

The extensive water is removed by the elevated temperatures in the spray drier chamber. As preceded, the optimal value of the chamber temperatures was a function of the other two factors. For its easy controllability, this factor was modified as the last one.

From this experiment, the *optimal combination of the three factors for the HA powder production* was determined: atomizer revolutions of 4,170 revolutions per minute ($\sim 10 \text{ Hz}$ atomizer frequency), slurry feedrate of 38.5 gmin^{-1} ($\sim 15\%$ pump rotations) and chamber temperature of 240°C (Table 28).

Table 28: Optimal setting of spray drier device for HA powder production

Spray drier parameter	Value
Input power	9.36 kW
Rotary disk diameter	50 mm
Inlet pipe diameter	4 mm
Atomizer frequency	10 Hz
Slurry feedrate	38.5 gmin ⁻¹
Inlet air temperature	240°C

The powder produced under such conditions (prior to all treatments) demonstrated the highest yield of the investigated combinations (> 750 g of HA from 16 l of the slurry) with the resulting average particle size measured as $35.09 \pm 10.87 \mu\text{m}$. The color of the produced powder was snow white.

To further increase the yield of the process, the HA powder stuck to the chamber walls was collected into separate containment and subjected to a thorough ball-milling procedure (100 RPM, 900 min). This powder was added into the batch prior to sieving.

4.1.2 Titanium dioxide

The general properties of TiO₂ were provided in section 2.2.2.3. Like HA powder, it was *necessary to select a powder with good flowability and suitable particle size range*.

Three commercially available TiO₂ powders were purchased: Titanium(IV) Oxide mesh - 325 (Sigma Aldrich), 5 – 20 μm TiO₂ (Itair Technologies) and *Amperit 782.001* (H.C. Starck, Inc., Newton, USA). The suitability of the powders was tested using various techniques (XRD, SEM, EDX and particle size analysis).

The notation ‘mesh -325’ corresponds approximately to less than ~ 44 μm particle sizes. However, the particle size analysis revealed the Sigma Aldrich titania consisted of three sub-portions having three dissimilar particle sizes: a dust of average particle sizes < 1 μm , and two powders of average sizes around ~ 40 μm and ~ 100 μm . The dust sub-portion was not successfully removed from the sieved powder, resulting in bad flowability of the powder and frequent choking in the SG-100 gun.

The experimentally discovered good flowability of the Itair technologies 5 – 20 μm titania was confirmed by SEM characterization as the acquired images showed spherical nature of the

particles. The powder particles cross-section images revealed doughnut-like structure of each particle, with the diameter of the inner cavity reaching almost 50% of the diameter of the particle. The particle size analysis validated the notation of the powder, with the average particle sizes between 4 – 24 μm . As given in detail in 2.1.2.5, particles of different radii develop different in-flight properties. The potential problem of using this powder is the disproportion of the particle sizes within the range (relative particle sizes up to 6x within the range), which could results in considerably different temperature and velocity of the particles within the jet. For the reasons, the Itair Technologies and Sigma Aldrich titania powders were not used.

According to the manufacturer, the *782.001 Amperit powder was specially developed for plasma spraying*. The indicated average particle size of the powder was 22 – 45 μm , as confirmed by subsequent particle size analysis. The purity of the powder as provided by the manufacturer is > 99.45% (Table 29). In this study, the powder was used for both plasma and cold spray experiments.

Table 29: As-indicated TiO_2 chemical analysis

Chemical characteristics		SiO_2	Fe_2O_3	TiO_2
Max. mass fraction	[%]	0.30	0.25	balance

As the powder was used for all the experimental work, a detail description of the modifications and processing and characterization of its properties will be provided in 4.2. The color of the powder prior to treatments was dark grey.

4.2 Powders Processing and Characterization

The in-house produced HA and purchased TiO_2 *powders were then processed to improve their properties and suitability for the spray processes*. After processing, the *final powder feedstock was thoroughly investigated* using various characterization techniques.

4.2.1 Powder Processing

Due to a precipitation nature of the HA preparation method and a low temperature characteristic for the processes, the resulting crystals are nanometric sizes and their mutual coalescence into bigger agglomerates is poor. This weak bond strength of the nano-particles could lead to splitting of the agglomerates when sprayed, resulting in high evaporation ratio

and low deposition efficiency. To improve the mutual coalescence of the particles, the *HA powder was heat treated* at 950 °C for 120 min in the air atmosphere and cooled down for 600 min to reach the ambient temperature. Due to the humid atmosphere, the powder was slightly wet prior to treatment, resulting in sputtering of the powder in the furnace. To suppress this effect, the powder was pre-dried at 160 °C for 60 min prior to the main heat treatment.

Particle size analysis of the HA powder prior to and after the heat treatment showed there was no significant difference in the average particle sizes. However, the heat treatment improved the strength of the chemical bond of individual grains, resulting in their better mutual coalescence and therefore superior suitability of the powder for thermal spray processing.

Along with the increase in the mutual coalescence of the particles, the *crystallinity of the HA powder increased*, as indicated by narrower and higher peaks in the measured XRD pattern. The heat treatment also *transformed other calcium phosphate phases into HA*, as indicated by the XRD and EDX measurements.

The heat treated HA powder turned cyan/light blue. This could be caused by the presence of manganese ions or other transition elements located in the crystal lattice structure [222].

Similarly, the *TiO₂ powder was heat treated*. As the mutual coalescence of the nanocrystals is guaranteed, the heat treatment parameters (temperature and time) were set *to induce phase transformations* in the powder so as to obtain a maximum proportion of rutile phase [224]. To transform anatase and brookite phases into rutile, the heat treatment was carried out at 750 °C for 120 min in the air atmosphere. The transformation was confirmed by the subsequent XRD analysis. The heat treated TiO₂ powder turned ochre/yellowish grey.

One of the crucial parameters of the powder feedstock influencing the in-flight particle properties is the *average size of the particles and the range of the particles* entering the plasma jet (2.1.2.5). For instance, a particle of twofold diameter has 8x bigger volume and mass, resulting in completely different behavior in the plasma jet when inserted. The influence of the powder feedstock particle size on the in-flight properties was studied thoroughly in the literature and is not a part of this study. As this factor was not studied, it was necessary to eliminate its effect.

To achieve better uniformity of the results obtained in the spray process and to lessen their variance, a *thorough sieving of both the powders was carried out* (Fritsch Analysette 3 sieve shaker). The standard batch sieving process was altered and a continual sieving was carried out instead: using the plasma system powder hopper feeding device, small flow of the powders was continually added into the column of the sieves (75 μm , 63 μm , 53 μm , 45 μm and 32 μm). Using a resin for specimen preparation and a dense lubricant, the sieves were hermetically bond together and a compressed Ar gas circulating from the top to the bottom of the column was used to aid in the sieving process (a hole was drilled into the bottom part of the column to ensure argon gas exhaustion; to suppress any powder losses, the hole was blocked using semi-permeable plastic sheet). The sieving was carried out at least for 10 hours for each 150 g of the powder (HA and TiO_2). Two sets of sieves were used to avoid mutual contamination of the two powders and thorough disassembling and cleaning of the sieves was carried out for every 450 g of the respective powder.

The powder was collected and only the particle size range 32 – 45 μm particle size range was used for further experiments. The bigger particles were then added to the powder collected from the spray drier walls and subjected to the ball-milling procedure. The obtained crushed powder was then re-sieved to improve the production yield.

4.2.2 Powder Characterization

Characterization of the processed powders was carried out. The details of the characterization techniques were provided in respective sections of 3.2.2 and 3.2.3.3. Inevitable differences in the standard procedures due to different nature of powders and coatings will be given in detail in respective sections of this chapter.

4.2.2.1 Phase Composition

The *phase and element composition* of the HA and TiO_2 powders was assessed using the XRD (Rietveld analysis) and EDX methods.

The *XRD spectra* were measured three times for each of the powders and average values were calculated as the acquired spectrum. Fig. 4-1 and Fig. 4-2 show the measured spectra of the powders along with the pure-material XRD spectra predictions as calculated in PowderCell software (3.3.3.1).

Powder Feedstock

Fig. 4-1: XRD spectrum of produced HA powder

Fig. 4-2: XRD spectrum of TiO₂ powder

The spectra calculated by PowderCell software correspond to the major XRD peaks predicted in 2.2.2.2 and 2.2.2.3 as could be seen from Table 30.

Powder Feedstock

Table 30: Theoretical and calculated major XRD pattern peaks for pure HA and TiO₂ powders

Prediction		HA			TiO ₂		
Theory	Intensity	100%	60%	60%	100%	50%	41%
	2θ [deg]	31.773	32.902	32.196	27.446	54.322	36.085
PowderCell software	Intensity	100%	63%	49%	100%	51%	44%
	2θ [deg]	31.761	32.893	32.192	27.433	54.312	36.079

For calcium phosphates, the most undesirable phase in terms of coated implant acceptance and good service life is calcium oxide, CaO. Generally, the HA powders produced by wet chemical synthesis method contain certain amount of other phases. Presence of CaO compound is usually indicated by presence of a small peak at $2\theta = 37.35^\circ$ (main peak of CaO diffraction pattern). Absence of the peak in the measured spectrum (indicated by the dashed line in Fig. 4-1) suggest *low content of the CaO phase*. The produced and processed HA powder was therefore pure with little contamination, as confirmed by subsequent Rietveld analysis.

Traces of impurities were present in the purchased TiO₂ powder (Fig. 4-2). A *small amount of anatase phase* was present in the powder as well as traces of hematite, Fe₂O₃ (as indicated by the manufacturer, Table 29).

Rietveld analysis of the measured XRD patterns stated the *phase composition of both powders*. Various calcium phosphate phases were considered into the calculations of the HA XRD pattern (annotation in Table 9). For TiO₂, three phases were considered (rutile, anatase, brookite) as well as the two impurities indicated by the manufacturer (hematite Fe₂O₃ and quartz SiO₂). The results of the Rietveld analysis could be seen from Table 31 and Table 32.

Table 31: Rietveld analysis of HA powder XRD spectrum

Phase	HA	CaCO ₃	CaO	α-CPP	β-CPP	Ca(OH) ₂	α-TCP	β-TCP	TTCP
Content [%]	93.0	5.0	1.0	1.0	0.0	0.0	0.0	0.0	0.0

Table 32: Rietveld analysis of TiO₂ powder XRD spectrum

Phase	rutile	anatase	brookite	Fe ₂ O ₃	SiO ₂
Content [%]	91.0	4.0	0.0	4.0	1.0

The numerical processing of the measured spectra validated the results obtained by XRD measurements. It was confirmed that the used powders *are pure with some small contamination of other phases only*. Presence of the detrimental CaO phase was suppressed in the produced HA powder and presence of other metastable phases (TCP, TTCP) was

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negligible. Presence of CaCO_3 phase would lead to prospective decrease in the Ca/P ratio, calculated as 1.67 for pure crystalline HA. The decrease was confirmed using EDX technique. It was found that the titania powder contains higher amount of hematite than indicated by the manufacturer as well as some small amount of anatase phase. However, the overall quality of the powder was sufficient for the subsequent plasma and cold spray experiments.

To aid in determination of the powders composition, *EDX technique was employed*. Both weight and atomic percentages of the powders were monitored. To detect the *changes in powder composition during the heat treatment*, the EDX measurements were carried out on the powders prior to and after the processing (Table 33, Table 34).

Table 33: EDX measurement of HA powder

HA powder	Weight %			Atomic %		
	Ca	P	O	Ca	P	O
As-produced	24.55 ± 2.07	8.43 ± 2.14	67.02 ± 0.94	12.08 ± 1.07	5.36 ± 1.35	82.56 ± 0.70
Heat treated	40.95 ± 1.08	18.87 ± 0.94	40.18 ± 0.14	24.67 ± 0.72	14.71 ± 0.69	60.62 ± 0.03

Table 34: EDX measurement of TiO_2 powder

TiO_2 powder	Weight %		Atomic %	
	Ti	O	Ti	O
Purchased	60.63 ± 8.06	39.37 ± 8.06	34.48 ± 7.61	65.52 ± 7.61
Heat treated	58.31 ± 11.35	41.69 ± 11.35	32.72 ± 10.66	67.28 ± 10.66

The EDX characterization revealed that the *heat treatment improved the overall quality* of the produced *HA powder*. The Ca/P ratio of the treated powder (slightly higher than 1.67 due to presence of CaCO_3 and CaO) was measured as $\text{Ca/P} = 1.68$, indicating only minor contamination of the powder, as compared to the value of 2.25 prior to the heat treatment. The values of the EDX measurement are not exact as hydrogen atoms could not be detected. Minor changes in the composition of TiO_2 powder were detected. However, relevant conclusions cannot be made due to the magnitude of the standard deviations of this measurement.

Both HA and TiO_2 powders used for the subsequent experimental work were of high purity and with composition close to their respective stoichiometric counterparts. The heat treatment aided in removing and changing detrimental or undesirable phases and, in the case of the HA powder, should result in increased particle coalescence and higher deposition efficiency.

4.2.2.2 Powder Microstructure

To further improve the insight into the *structure and character of the used powders and to investigate the shape and morphology of the powder particles as well as the inner structure of the particles*, an SEM analysis was performed.

Observations of the produced *HA powder* prior to sieving revealed the *shape of the particles changes as the particles sizes varies*. Almost 95% of the particles smaller than 32 μm are strictly spherical, whereas there's an increasing tendency of loosing shape regularity towards bigger particle sizes. Spherically shaped hydroxyapatite particles with diameter bigger than 60 μm were rarely found and there were no regularly shaped particles bigger than 70 μm . Fig. 4-3 illustrates this phenomenon.

Fig. 4-3: Shape changes of the HA particles with increasing average size

This distinct trend could be explained by differences in particles aerodynamic resistances when spray dried. As the size of the produced particles is relatively small (i.e. less than 100 μm), their aerodynamic resistance is highly influenced by their respective sizes. The smaller particles dwell within the spray drier chamber swirl for a longer time and their shape is changed into spheres due to the influence of wind flux. On contrary, the bigger particles do not remain in the hot air flux long enough to be totally spheroidized, their shape therefore differs

from perfect spheres. For the particle size range selected for the deposition experiments (32 – 45 μm), the regularity of the shape was sufficient, resulting in good powder flowability.

SEM image analysis of the heat treated and sieved HA powder (Fig. 4-4) *confirmed the reliability and efficiency of the sieving process* and corresponded well with the results of subsequent particle size analysis.

Fig. 4-4: SEM images of used HA powder under various magnifications

The surface of the HA particles displayed negligible roughness and presence of minor irregularities on the particle surfaces, presumably a consequence of the precipitation nature of the powder production. *Spherical character of particles was confirmed.*

The *SEM observations confirmed the indicated particle sizes of the as-purchased TiO_2 powder* as there was no significant difference in the average sizes prior to and after the sieving procedure. This was confirmed by the conducted particle size analysis.

Contrary to the produced HA powder, the character of the *titania powder* particles was *strictly angular* (Fig. 4-5), probably a consequence of the production technology. The character of the particles presumably originated in crushing of the powder, initially indicated as ‘fused’. This idea is supported by the fact that cleavage facets of brittle fracture could be seen

on the particle surfaces at higher magnifications. Despite the angular character of the particles, the flowability of the selected titania powder was good.

Fig. 4-5: SEM images of used TiO_2 powder under various magnifications

To further improve the knowledge on the powders used in this study, an *SEM analysis of powder cross-sections* was carried out. The metallographic preparation of the powders cross-sections could not follow the procedure described in 3.2.2.2 due to insufficient bond strength of the resin compound. Frequent peel off of the powder particles was observed during subsequent grinding and polishing. Instead, the powders were mounted into two component compound used for preparation of TEM samples, which has proven superior bond strength and lower powder peel-off. Ten parts of resin (601.07270 Epoxy Resin G-2, Gatan, Inc., Pleasanton, USA) were mixed with one part of hardener (601.07270 Epoxy Hardener G-2, Gatan) and allowed to undergo proper curing (130 °C, 10 min). After curing, the samples containing the fine powders were ground following the standard procedure.

The cross-section observation revealed a *porous structure of HA and TiO_2 powders* (Fig. 4-6 and Fig. 4-7).

Fig. 4-6: SEM images of used HA powder cross-section under various magnifications

Fig. 4-7: SEM images of used TiO₂ powder cross-section under various magnifications

The internal porosity of HA powder could be caused by the spray drying procedure where the surface of the atomized particles gets dry and subsequent drying and contraction of the

slurry material within the particle creates the internal porosity. The source of the porosity of titania powder is unknown, most likely a result of the fusion process in the production of the powder. The SEM observed internal porosity of the powders could not be determined using the image analysis method (particle size below method resolution threshold, 3.2.2.4). The helium pycnometric method was used to assess the accurate values.

4.2.2.3 Porosity

The porosity of the powders was measured using the pycnometric method. As this method measures *internal porosity* only, the open porosity of the particles was not assessed. Details of the method are given in detail in 3.2.2.4.

Comparison of the measured powder density with the theoretical values of mass density allowed determination of the powders porosity (Table 35). It was found that the fused TiO₂ powder has a slightly higher level of internal porosity as compared to the produced HA powder.

Table 35: Internal porosity of HA and TiO₂ powders

Powder	Density [gcm ⁻³]		Porosity [%]
	measured	theoretical	
HA	2.904 ± 0.005	3.156	7.99
TiO ₂	3.671 ± 0.000	4.250	13.62

4.2.2.4 Particle Size Analysis

To evaluate the effectiveness of the sieving process and to obtain information on the average particle size of the used powders, a *particle size analysis* was carried out.

The measurement procedure is given in detail in 3.2.3.3. It was found that the HA powder was sieved thoroughly (Fig. 4-8). The total amount of HA dust (i.e. particles < 2 µm) was approximately 2.2%. Also it was found that the majority of the obtained HA powder was within the selected 32 – 45 µm range. The numerical results of particle size analysis stated the *average HA particle diameter* as $d_{HA} = 39.90 \pm 10.61 \mu\text{m}$.

The measurements of TiO₂ powder confirmed the narrow range of the processed powder (Fig. 4-9). There was no powder dust present in the sample and the powder particles average sizes were in good agreement with the selected range. The exact results of particle size analysis calculated the *average TiO₂ particle diameter* as $d_{TiO_2} = 32.20 \pm 8.88 \mu\text{m}$.

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The results obtained using the particle size analysis method *corresponded with the precedent SEM observations and confirmed high efficiency of the sieving process*. The particle size range of the processed powders was sufficiently narrow in order to unify the results of the in-flight powder properties and lessen the prospective variances.

Fig. 4-8: Particle size analysis of used HA powder

Fig. 4-9: Particle size analysis of used TiO₂ powder

CHAPTER 5: IN-FLIGHT PROPERTIES

A major part of the experimental work within this study was devoted to *measurements of in-flight properties of deposited powders*. The measurements of average particle temperatures and velocities were carried out using SprayWatch & Hi-Watch systems (3.2.1.1) and tailored to the needs of two experimental approaches: the *OAT method* provided basic information needed to uncover the nature of the relations while the *Taguchi design* offered an alternative concept for the measurements. To characterize the entire process of deposition, the results of the measurements were supported by performed *regression analysis* and *software simulations*. The results contributed for selection of the six combinations used for studying of coating properties (3.2.2). Due to limitations, the in-flight measurements were conducted for plasma spray process only.

5.1 One-At-A-Time Method

'*Several parameters, one at a time*' method (3.2.1.2) provides a simple way of assessing influences of the selected plasma spray parameters (PSP) on the properties of a powder during the deposition process.

Based on trial runs, the ranges for every PSP and the steps between two levels of each PSP were selected to affect all potential phenomena. *Influences of the selected PSP on the average temperature and velocity of particles* were measured for HA and TiO₂ powders. The results were then mutually compared to facilitate *initial comparison on the relative prominence of every PSP* and strength of their respective influence.

5.1.1 Particular Parameter's Influence

5.1.1.1 Hydroxyapatite

The influence of the six PSP on the in-flight temperature and velocity of the HA powder particles could be seen from Fig. 5-1.

The influence of *net power* (NPW) parameter on the mean particle *temperature* follows a phenomenon described in 3.1.1.1. The increase in net power initially gives rise to higher temperature of particles. However, as the velocity of the particles also increases, shorter dwelling times of the particles in the jet result in a reduced heat transfer and, subsequently, drop in the temperature for higher values of net power (around 10 kW). However, the

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magnitude of this effect is relatively small: the difference between maximum and minimum values is around 30 K, i.e. within an error range of a single measurement.

Fig. 5-1: Influence of selected PSP on in-flight properties, HA powder, OAA method

Net power was expected to be one of the factors with major influence on particle *velocities*. This was confirmed through experiments, as seen from Fig. 5-1. The higher the power, the higher the mean velocity of the particles. The linear change from 204 ms⁻¹ to 306 ms⁻¹ was observed when changing the net power values from 7 kW to 15 kW.

In contrast to expected results, the *temperature* profile has a rising tendency with increasing *flow of main gas* (MGF). The purified argon gas used for the experiments is considered to be a heavy-ions momentum transmitter rather than temperature transferring

medium. However, the measured trend in particle temperatures with varying main gas flow is clearly increasing: the temperature has risen from 2378 K to 2462 K with increase in MGF from 40 to 100 scfh. The character of the temperature curve appears to be rather steady at lower argon flows (below 60 scfh), whereas there is a clear rising trend for the higher values. The expected influence of *main gas flow* on the *velocity* of particles was confirmed by the experiment. An increase in the mean velocity by 70 ms^{-1} was observed for the increase of 60 scfh.

Good thermal transfer properties of light gases cause immediate and superior heat transfer. As helium was used as an *auxiliary gas* (AGF), rising *temperature* trend was expected with increase in its flow. This tendency was experimentally proven. However, as seen from Fig. 5-1, with the difference of 60 scfh in the helium flow (20 – 80 scfh), the temperature of HA particles has risen by 39 K only. This value falls within the error range of a single measurement and therefore cannot be considered as a clear trend. As compared to the effect on the mean temperature, the effect of the *auxiliary gas flow* on the mean *particle velocity* is significant. Apparent rise of $229 - 293 \text{ ms}^{-1}$ was observed for the increase in the auxiliary gas flows from 20 scfh to 80 scfh.

The existence of carrier gas effect (2.1.2.5) frequently observed for external powder feeding is normally suppressed by the inwards injection of powder particles. As the plasma SG-100 Praxair gun used for the experiments (Appendix A) has the internal powder feeding nature and, furthermore, the standard anode was replaced by angle feeding anode, the effect was expected to be virtually non-existent. However, the results of conducted experiments showed the inner construction of SG-100 Praxair plasma gun does not prevent the phenomenon from arising. The *carrier gas phenomenon occurs notably*, creating a peak in both the temperature and velocity curves. The differences between the maximum and minimum values of HA particles temperature and velocity were 174 K and 36 ms^{-1} , respectively. The successful detection of the carrier gas effect justified the selection of the total range and the gap between the levels of the carrier gas flow (CGF).

It was shown that the *powder feed hopper system revolutions per minute* value (RPM) affects the amount of powder inserted into the jet significantly (Appendix Fig. 2). The effect of

rising amount of powder entering the plasma jet consists in the fact that the same amount of the plasma heat and momentum are transferred to a higher number of particles. A decrease in both the average temperature and velocity values was therefore expected with increasing amount of HA powder. As seen from Fig. 5-1, the declining trend was confirmed experimentally. The *temperature* dropped by 69 K while the *velocity* dropped by 22 ms^{-1} with change in the RPM from 1 to 4. According to the conversion experiment conducted to estimate the amount of powder entering the jet for various combinations of RPM and CGF (Appendix A), the amount of the HA powder corresponded to 2.8 gmin^{-1} for 1 RPM and 7.9 gmin^{-1} for 4 RPM (for the fixed value of carrier gas flow of 12 scfh).

The last factor investigated was the distance between spray gun nozzle and the detection volume center. The *spray distance factor* was experimentally proven to have the highest impact on both *particles temperatures and velocities*. Altering the spray distance from 75 mm to 150 mm brought along a change in particle temperatures from 2674 K to 2312 K, i.e. a difference of 362 K. Concurrently, the average velocity of hydroxyapatite powder particles dropped from 341 ms^{-1} to 201 ms^{-1} .

5.1.1.2 Titanium dioxide

As HA and TiO_2 powders possess different properties, the investigated PSP could influence the *in-flight properties* in *dissimilar* ways. The conducted experiments confirmed this hypothesis (Fig. 5-2).

In case of *net power* influence on the temperature of particles, the phenomenon of decreasing *temperature* due to elevated velocity observed for HA powder does not occur as the trend in the temperature of the particles is clearly ascending. With the increase in net power from 7 kW to 15 kW, the temperature has risen from 2121 K to 2438 K, i.e. the difference of 317 K. Also, the average velocity of particles increased by 67 ms^{-1} , from 158 ms^{-1} to 225 ms^{-1} .

Temperature of TiO_2 particles decreased with increasing flow of argon gas. The increase in the flow from 40 scfh to 100 scfh was followed by a drop in the temperature from 2621 K to 2438 K (difference of 183 K). This fact is in accordance with the momentum transmitting theory described earlier (2.1.1.1). The heavy argon ions were expected to give rise to the TiO_2

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mean *velocity of the particles*. The relative magnitude of this increase was not as significant: an increase of 29 ms^{-1} was observed.

Fig. 5-2: Influence of selected PSP on in-flight properties, TiO_2 powder, OAA method

Increasing flow of the auxiliary helium gas resulted in lower average *temperatures of TiO_2* (a drop from 2473 K to 2438 K). Opposite trend was expected as helium is a good heat transmitter. The declining trend in temperatures could be caused by slightly increasing *velocity of the particles* (an increase from 216 ms^{-1} to 227 ms^{-1}). Both the trends are weak, differences of 35 K and 11 ms^{-1} lie within areas close to measurement error ranges. Due to this fact, the measured data cannot be considered as clear trends.

The measurements of the effect of *carrier gas flow* on *temperature and velocity of the particles* indicated the existence of the carrier gas effect: the maximum values of 2470 K and 237 ms⁻¹ occur for middle levels of CGF, while minimum values of 2422 K and 225 ms⁻¹ occur at selected range limits. Both differences are, however, negligible and fall within an error range of the SprayWatch system and fluctuation in the generated plasma jet.

The discovered effect of the powder feed hopper system *revolutions per minute* followed previous observations. According to the conversion experiment (Appendix A), the quantity of TiO₂ powder entering the plasma jet amounts to approximately 5.9 gmin⁻¹ at 1 RPM and 23.8 gmin⁻¹ at 4 RPM, i.e. approximately fourfold increase. Both the average *temperature and velocity* dropped by 117 K and 23 ms⁻¹, respectively (Fig. 5-2), the effect was therefore more significant for temperature measurements.

The influence of *spray distance* factor was proven to significantly influence the measured in-flight properties. With the increase in spray distance from 75 mm to 150 mm, the mean *temperature of TiO₂ particles* dropped from 2561 K to 2290 K while the mean *velocity* dropped from 242 ms⁻¹ to 193 ms⁻¹ (271 K and 49 ms⁻¹ in terms of differences)

Mutual *comparison of the results of OAAT experiments with HA and TiO₂ powders* showed that the standard deviations of the measurements are higher for HA powder. This fact is caused by higher scattering of HA powder as compared to heavier TiO₂ particles and is in good agreement with previous experimental work (Appendix A).

Table 36 summarizes the maximum and minimum values of temperature and velocity of the particles reached within the OAAT experimental work. A negative sign in the difference column indicates a declining trend in the measured curve.

Table 36: Mutual comparison of HA and TiO₂ powders, OAAT design

Parameter	Temperature [K] (HA/TiO ₂)			Velocity [ms ⁻¹] (HA/TiO ₂)		
	Min	Max	Difference	Min	Max	Difference
Net power	2510 / 2121	2540 / 2438	30 / 317	204 / 158	306 / 225	102 / 67
Main gas flow	2378 / 2438	2462 / 2621	84 / -183	212 / 197	282 / 226	70 / 29
Auxiliary gas flow	2405 / 2438	2444 / 2473	39 / -35	229 / 216	293 / 227	64 / 11
Carrier gas flow	2436 / 2422	2610 / 2470	174 / 48	260 / 225	296 / 237	39 / 12
Hopper revolutions	2470 / 2457	2539 / 2574	-69 / -117	267 / 220	289 / 243	-22 / -23
Spray distance	2312 / 2290	2674 / 2561	-362 / -271	201 / 193	341 / 242	-140 / -49

As could be seen, the *velocities of TiO₂ particles were slightly lower than those of HA particles*. As the average particle size of both powders is similar (4.2.2.4), this fact could be caused by different mass density of the powders. Due to higher moment of inertia, the heavier TiO₂ particles are more resistant to a change in their respective velocity vector and it is more difficult to transfer the momentum from the jet to the particles (this trend was subsequently confirmed using the Taguchi method, 5.2). The six investigated PSP exhibit an analogous influence on the velocity of particles of both powders and the magnitude of the effect appears stronger for HA particles. The measured *temperatures of both powders appear equivalent* and there are no distinct differences in the reached values. Magnitude of all effects on the measured temperatures differs and cannot be unambiguously determined.

The different trend in NPW influence could be explained by the difference in the reached velocities. While the velocities for HA powder reached higher values and the shortened dwelling time in the plasma jet resulted in lowering of the temperature, the velocities of TiO₂ particles did not reach values high enough for this effect to occur. There was an increase in velocities of both powders with an increase in both MGF and AGF. However, the increase in the mean velocities of TiO₂ powder was negligible. This difference, along with diverse thermal properties of both powders (a dissimilar heat intake influenced by the values of specific heat, latent heat and particularly thermal conductivity, Table 27) could be a reason for dissimilar influences of both factors on the measured temperatures. The carrier gas effect observed for both powders was more intense for HA powder, in accordance with the lower density theory. The decrease in both measured in-flight properties due to changes in RPM parameter were confirmed for both powders. The decrease in temperature is slightly lower for HA powder and the velocities dropped equally. The influences of SPR factor are significant and in good accordance with the theory. All four SPR dependencies appear to follow linear trend, which was subsequently confirmed by performed regression analysis (5.3.1).

5.1.2 Overall Relative Influence

OAAT method does not allow determining importance of a particular PSP as compared to influences of other PSP. Due to impossibility of transferring the selected value ranges for diverse PSP, it is impossible to specify the relative weight of particular factors influencing the

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in-flight velocity and temperature. Essential *overview on single PSP importance* could be created, though. Fig. 5-3 provides a summary of the relative importance of the six PSP. It must be noted that this overview is influenced by the particular PSP selected ranges and the inequality of number of levels per each PSP.

Fig. 5-3: Relative influence of investigated PSP on in-flight properties, OAAT method

For the value ranges selected for the purposes of OAAT method, the *most influential factors* are spray distance for HA and net powder for TiO₂ powders, respectively. With increase of 100% in spray distance (75 mm to 150 mm), the temperature and velocity of HA dropped by 14% and 41%, respectively. With the increase of 114% in net power (7 kW to 15 kW), the temperature and velocity of TiO₂ particles increased by 13% and 30%, respectively.

For HA powder, *net power* relatively high influence on the mean velocity (33%) is a possible reason of the factor's negligible influence on the mean temperature.

Both *MGF* and *AGF* partially influence the average velocities: with the increase of 150% (argon) and 300% (helium) in their respective flows, the velocities changed by 25% and 22% (HA) and 13% and 5% (TiO₂). The influence of both factors on the temperature of particles is

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of different nature: an increase of 3% and 2% was observed for HA powder while a decrease of 7% and 1% was measured for TiO₂. The values are, however, too small to be considered a distinguished trend.

As *CGF* influence was proven to remain peak-type dependence in spite of using inwards powder injection. For HA, the maximum difference reaches 7% for temperature and 13% for velocity.

The hopper system *RPM* parameter was proven to have an effect on the powder in-flight characteristics. With the increase in the revolutions of 300% (1 RPM to 4 RPM), the observed decrease in temperature reached 3% (HA) and 5% (TiO₂) while the velocity dropped by 8% (HA) and 9% (TiO₂).

Spray distance (*SPR*) was the second most influential factor for TiO₂ powder. With the increase from 75 mm to 150 mm, the temperature and velocity of the particles dropped by 11% and 20%, respectively.

Additional calculations were performed to enable *mutual comparison of the influences of the investigated PSP*. Data in Table 37 show relative changes in the mean temperature and velocity of both powers with a theoretically re-calculated 100% accrual of all PSP ranges. The hypothetical calculations were based on the results provided by subsequent regression analysis, assuming intrinsic dependence type for each PSP. The peak dependencies of NPW influence on HA temperature and all CGF influences were re-calculated based on the extreme values of given peak (indicated by asterisk).

Table 37: Hypothetical re-calculation of particular PSP influences with 100% change in PSP value

Parameter	Re-calculated ranges (HA/TiO ₂)		Temperature change [%]	Re-calculated ranges (HA/TiO ₂)		Velocity change [%]
	at min	at max		at min	at max	
NPW [kW]	5 / 7	10* / 14	2 / 12	7 / 7	14 / 14	31 / 28
MGF [scfh]	50 / 100	100 / 50	4 / 5	40 / 40	80 / 80	21 / 10
AGF [scfh]	20 / 80	40 / 40	0 / 1	20 / 20	40 / 40	12 / 2
CGF [scfh]	16 / 6.5	8* / 13*	9 / 2	5 / 4.5	10* / 9*	9 / 5
RPM [1]	4 / 4	2 / 2	1 / 2	4 / 4	2 / 2	5 / 6
SPR [mm]	150 / 150	75 / 75	14 / 11	150 / 150	75 / 75	36 / 20

The assumptions and methodology used for the re-calculations disallow the values to be taken as absolute. However, the calculations highlighted the influences of important factors. It could be concluded from Table 37 that the factors most influencing the temperature of the particles are spray distance (14% for HA / 11% for TiO₂) and net power (12% for TiO₂) and the factors influencing the velocity of the particles are net power (31% for HA / 28% for TiO₂), spray distance (36% for HA / 20% for TiO₂) and main gas flow (21% for HA / 10% for TiO₂).

5.2 Taguchi Design of Experiment

Taguchi design of experiment (3.2.1.3) provides an alternative approach to study the process of plasma deposition and to measure the in-flight properties of the powder particles.

Eighteen experimental runs were conducted for each of the powders, each run carried out two times to improve the reliability of the results. The measured results were used for *plotting method* (5.2.1), *analysis of variance* statistical processing (5.2.2), *factor interactions determination* (5.2.3) and to determine the *relative influences* (5.2.4). The conducted runs provided the data necessary to select six representative samples for coating production.

Table 38 shows the numerical results of the in-flight properties of the HA and TiO₂ powder particles according to the Taguchi design including the calculated deviations. The respective levels of the particular plasma spray parameters of the 18 sets could be seen from Table 17.

Graphical plot of the results could be seen from Fig. 5-4 and Fig. 5-5, respectively. The six PSP combinations selected for the subsequent coating production are included in the charts. The respective standard deviations of particular measurements are not included in the plots in order to retain lucidity.

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Table 38: In-flight particle temperatures and velocities, Taguchi design

Taguchi run	Temperature [K]		Velocity [ms ⁻¹]	
	HA	TiO ₂	HA	TiO ₂
01	2524 ± 28	2727 ± 6	175 ± 3	151 ± 0
02	2495 ± 22	2277 ± 21	188 ± 4	141 ± 0
03	2475 ± 44	2125 ± 6	203 ± 22	137 ± 0
04	2361 ± 23	2600 ± 12	160 ± 20	146 ± 1
05	2470 ± 5	2444 ± 14	275 ± 11	174 ± 0
06	2589 ± 6	2388 ± 13	264 ± 6	196 ± 2
07	2437 ± 7	2617 ± 1	214 ± 10	159 ± 0
08	2350 ± 27	2449 ± 2	236 ± 2	193 ± 1
09	2500 ± 36	2592 ± 15	243 ± 7	193 ± 3
10	2540 ± 41	2267 ± 13	175 ± 14	134 ± 1
11	2453 ± 86	2212 ± 16	171 ± 15	127 ± 2
12	2724 ± 69	2373 ± 14	248 ± 9	176 ± 1
13	2370 ± 40	2381 ± 14	172 ± 10	150 ± 1
14	2633 ± 18	2830 ± 5	287 ± 5	201 ± 0
15	2514 ± 5	2344 ± 19	204 ± 6	173 ± 1
16	2451 ± 4	2593 ± 1	244 ± 25	176 ± 1
17	2415 ± 7	2560 ± 6	199 ± 21	174 ± 2
18	2428 ± 10	2362 ± 8	229 ± 12	194 ± 0

Fig. 5-4: In-flight properties of HA powder, Taguchi design

Fig. 5-5: In-flight properties of TiO_2 powder, Taguchi design

5.2.1 Plotting method

Illustrative *plotting method* allows a convenient comparison with the results obtained according to OAAT design. However, minor differences are to be expected due to presence of factor interactions.

Graphical representation of the plotting method using measured in-flight data could be seen from Fig. 5-6. All investigated PSP are plotted for three different levels; each of the data points is an average value of 12 measurements.

5.2.1.1 Hydroxyapatite

Net power dependence shows rapid drop in *temperature* measurement with its value increase. A difference of -105 K was detected with a change from 7 kW to 15 kW. As the results of OAAT method indicated a steady trend in similar measurement, some interactions with other factors are anticipated. The increase in the average *velocity* of the particles was 34 ms^{-1} , smaller than the result obtained using OAAT design (102 ms^{-1}).

A rising flow of primary argon gas in the plasma system chamber was identified to have an effect on the *temperature and velocity* of the particles. With the change of 60 scfh, the former increased by 91 K while the latter increased by 42 ms^{-1} . This increase is in good accordance with OAAT measurements, where an increase of 84 K and 70 ms^{-1} was observed.

In-Flight Properties

The flow of auxiliary gas was proven to have an influence on both in-flight characteristics. Changing the helium flow from 20 scfh to 80 scfh induced a 45 K increase in *temperature* and 43 ms^{-1} increase in *velocity*. OAAT observations indicated increasing trend for the temperature (difference of 39 K) and superior increase in velocity (64 ms^{-1}), in good accordance with the Taguchi results. The main and auxiliary gas flows induce similar rise in the in-flight characteristics. Contrary to expected results, the argon atoms give rise to higher temperature as compared to helium atoms. The velocities induced by the gases flows are virtually identical.

Fig. 5-6: PSP influences, plotting method, Taguchi design

Descending trend was observed for argon carrier gas flow influence: with a change from 6 scfh to 15 scfh, the average *temperature* dropped by 49 K while the *velocity* decreased by 12 ms^{-1} . Peaks observed using OAAT method indicated a difference of 174 K and 39 ms^{-1} .

Changes in measured data due to feeding rate were too small (a drop of 29 K and 5 ms^{-1}) and the hypothesis of its influence on either *temperature or velocity* could be rejected. Despite different ranges used for measurements according to the two approaches (Taguchi 2 – 4 RPM, OAAT 1 – 4 RPM), this conclusion corresponds to the results obtained by OAAT.

The most significant changes in both *temperature* and *velocity* profiles occurred due to change of spray distance. With a change from 75 mm to 125 mm, the temperature dropped by 144 K and velocity dropped by 50 ms^{-1} . OAAT measurements indicated a drop of 362 K and 140 ms^{-1} with a change from 75 mm to a farther distance of 150 mm.

5.2.1.2 Titanium dioxide

Net power influence on the particles is in good accordance with OAAT observations as both mean *temperature and velocity* of the particles increased (198 K and 37 ms^{-1}) with increasing new power level. The values measured according to OAAT design were 317 K and 67 ms^{-1} , some interactions are therefore to be expected (corresponds to HA powder results).

The declining trend of the *temperature* (a drop of 167 K) for main gas flow factor is in agreement with the value obtained according to OAAT design (a drop of 183 K). Also the increase in the mean *velocity* of particles was confirmed, indicating good stability of both testing methods ($+25 \text{ ms}^{-1}$ for the Taguchi and $+29 \text{ ms}^{-1}$ for OAAT).

The increasing flow of auxiliary gas exhibited peak-type dependence with a maximum drop of 97 K in the *temperature* of the particles. OAAT indicated this trend as slightly declining, with a drop of 35 K. Due to existence of this discrepancy, some strong interactions are expected. An increasing trend in *velocities* was observed (a difference of 12 ms^{-1}), in accordance with OAAT method results (a difference of 11 ms^{-1}). Both values are, however, within a measurement error range.

As well as in OAAT design, the carrier gas effect was not confirmed by Taguchi design. Declining trends of the in-flight properties were observed: a drop of 128 K and 11 ms^{-1} were measured with a change of carrier gas flow from 6 scfh to 15 scfh. The differences between maximum and minimum values according to OAAT design were calculated as 48 K and 12 ms^{-1} . Some interactions with other factors (presumably RPM) could be expected.

The Taguchi measurement of *RPM* influence on the *temperature and velocity* of particles corresponds with the results of OAAT design: a drop of 99 K/117 K (Taguchi/OAAT) in the mean temperature and a drop of $16 \text{ ms}^{-1}/23 \text{ ms}^{-1}$ (Taguchi/OAAT) in the mean velocity indicate precise measurement and good repeatability of the measurement processes.

Increase of 50 mm (75 mm to 125 mm) in spray distance factor resulted in a decrease of 238 K and 21 ms⁻¹ in *particles temperature and velocity*, respectively. Analogous trend was observed in OAAT experiments: a drop of 271 K and 49 ms⁻¹ was measured. As the measurements obtained using both methods were similar for both powders, spray distance could be considered a parameter influencing particles in-flight properties independently on other factors, i.e. without respect to the values of other spraying parameters. This fact was confirmed by subsequent interaction analysis.

5.2.2 Analysis of Variance

The *ANOVA* statistical tool provided thorough examination of the results obtained according to the Taguchi design. It allowed detection of mutual interactions of the investigated PSP as well as determination of particular PSP influences.

Based on changes of the measured data variances due to different PSP levels compared to overall variation changes, ANOVA determined the credibility of measured data sets and respective PSP influences. Comparison of calculated F-ratio and table values for given degrees of freedom and significance level (Table 18) provided information on the overall effect of particular PSP on the observed in-flight characteristics.

Calculated F-ratios for all investigated PSP for both temperature and velocity profiles could be seen from Table 39 as well as variances of particular PSP (rounded values).

Table 39: Variances and F-ratios calculated using ANOVA, Taguchi method

Parameter	Variance				F-ratio			
	Temperature		Velocity		Temperature		Velocity	
	HA	TiO ₂	HA	TiO ₂	HA	TiO ₂	HA	TiO ₂
Net power	33390	136803	4609	4621	10.55	25.55	14.88	331.20
Main gas flow	27174	84394	6153	1971	8.59	15.76	19.87	141.27
Auxiliary gas flow	6151	29170	5771	434	1.94	5.45	18.64	31.14
Carrier gas flow	7144	50713	494	380	2.26	9.47	1.59	27.21
Revolution per minute	3040	36083	65	765	0.96	6.74	0.21	54.86
Spray distance	63936	187563	8215	1385	20.21	35.03	26.53	99.24
Error factor	3164	5354	310	14	-	-	-	-

To facilitate easier orientation in the results, the calculated F-ratios and respective table values could be seen from Fig. 5-7 for HA and TiO₂ powders, respectively (high F-ratios are

truncated at 10 to maintain lucidity). In case the calculated F-ratio is higher than the F-table value (Table 18), the selected PSP is deemed to have a significant influence on the process at a given confidence level. It is necessary to note that the relative magnitudes of the calculated and tabulated F-ratio do not signify the extent of the influence of a selected PSP.

Fig. 5-7: Calculated F-ratios of HA and TiO₂ powders, Taguchi design

5.2.2.1 Hydroxyapatite

Analysis of variances for different PSP levels showed a *significant influence of spray distance, Main gas flow and net power*. The influence of the three PSP was proven at highest confidence level (99%) and the parameters therefore have major impacts on both the in-flight properties of the particles. The influence of *AGF* on the velocity of the particles was also confirmed at 99% level. On the other hand, the hypothesis of auxiliary gas impact on the temperature was not confirmed at 90% confidence level. The influence of carrier gas flow factor on the particles (detected as peak-type dependencies in OAAT design) was not confirmed by ANOVA and the hypothesis of its influence was rejected at the lowest confidence level used (90%) probably due to constraints of the Taguchi design (three levels per particular parameter only). The idea of the influence of RPM factor on temperature and velocity of HA particles was rejected at the lowest confidence level.

5.2.2.2 Titanium dioxide

The hypothesis of PSP influence on the measured velocity was confirmed at 99% level for all investigated factors. For the temperature measurements, the characteristic were confirmed at the highest level (99%) except for auxiliary gas flow parameter: the hypothesis of the influence of AGF on the mean temperature of the particles was confirmed at 95% level, it was rejected at 99% level, though.

The major influence of net power and spray distance is in agreement with the results obtained using OAAT and the Taguchi plotting methods. The impact of main gas flow detected by ANOVA could be seen from the Taguchi plotting method measurements. The influence of auxiliary gas flow on the velocity of the particles for both powders confirmed at 99% corresponds to the previous results as well as the slightly lesser AGF impact on the measured temperature. The influence of RPM parameter was confirmed at 99% confidence level for TiO_2 powder, in contrast to HA powder. The difference between powders is in accordance with both OAAT and the Taguchi plotting methods results and is probably a consequence of different mass densities of the used powders.

5.2.3 Factor Interactions

In stochastic processes such as plasma spray, *interactions of the factors* influence the results. Differences in the graphical plots of OAAT and the Taguchi methods indicated potential existence of these interactions. In order to provide detail overview of the process of plasma spray, the interactions were investigated.

For interaction detection, mutual combinations of all investigated PSP were calculated. The values of every PSP were integrated at given level with respect to the three levels of another PSP. In combination with two investigated in-flight parameters and two powders used, a total of 540 combinations were calculated and plotted as parametrical three-data-point curves. Graphical plot of mutual slopes of the parametrical curves aided in evaluating the *intensity of the interaction* between the two investigated PSP.

Due to different nature of both powders, some differences in the calculated interactions were expected. This fact was confirmed as some interactions detected for HA powder were either negligible or non-existent for TiO_2 powder and vice versa.

5.2.3.1 Hydroxyapatite

The statistical procedure confirmed two strong (CGF and AGF, CGF and RPM) and some moderate interactions in *temperature measurements* (NPW and AGF, NPW and CGF, MGF and RPM, AGF and RPM). The interactions of net power factor were expected due to differences in OAAT and the Taguchi plotting methods as well as the interactions of carrier gas flow factor. Interactions of hopper revolutions per minute factor with all three gases flows

acknowledges the theoretical assumption of interaction as a consequence of different thermal and velocity properties induced by the gases to different amounts of powder entering the plasma.

For *velocity measurements*, two mediocre interactions were detected (AGF and CGF, CGF and RPM). Again, this result corresponds to the differences in OAAT and the Taguchi plotting method results. The influence of the interactions on the velocity of the particles acquired in the jet are weaker than their effect on the temperature of HA particles.

There was no indication of interaction between main and auxiliary gases flows and no interaction was detected between net power and main gas flow in both in-flight characteristics. Spray distance was confirmed to be an independent factor as there was no interaction of this parameter with any of the remaining PSP.

The mutual interferences of other PSP were negligible.

5.2.3.2 Titanium dioxide

Different situation occurred in case of TiO₂ powder interactions calculations. Some interactions detected for HA powder were not explicitly confirmed for TiO₂ and their relative magnitude changed eventually.

For influence of investigated PSP on the *temperature of the particles*, three mediocre (MGF and CGF, MGF and RPM, AGF and RPM) and three minor (NPW and MGF, NPW and RPM, CGF and RPM) *interactions* were detected. As well as in the case of HA powder, the interactions of net power factor were expected due to differences in OAAT and the Taguchi plotting methods. In contrast to the theoretical hypothesis based on the results of OAAT and the Taguchi plotting methods, no interaction was detected for auxiliary gas flow factor apart from the mediocre interference with hopper revolutions.

In case of the mutual concurrence of the factors on the in-flight *velocity*, five *minor interactions* were detected (NPW and CGF, MGF and AGF, AGF and CGF, AGF and RPM, CGF and RPM). Both the net power and carrier gas flow interactions were expected based on the previous results as well as the interaction between carrier gas flow and hopper revolutions.

The interaction between main and auxiliary gases flows was confirmed for velocity measurements. However, the interaction was weak as compared to the other PSP interactions.

In-Flight Properties

As well as for HA, there were no interactions detected for spray distance parameter, in accordance with the previous experimental results.

The discovered mutual interactions of the investigated PSP aided in theoretical description of the deposition process using governing equations (5.3.2). The negligible interferences of the PSP were not considered into the regression analysis.

5.2.4 Relative Factor's Influence

Statistical ANOVA method allows *determination of particular PSP influences* on the overall changes in in-flight properties. Comparing values of individual PSP sum of squares with the overall values provides basic information on respective weight of parameters.

The sum of squares values could be seen from Table 40 as well as percentage contribution of particular PSP (rounded values). It must be noted the percentage contribution was calculated for selected PSP level ranges and its validity is therefore limited within the selected bounds.

Table 40: Relative contribution of investigated PSP

Parameter	Sum of squares value				Relative influence [%]			
	Temperature		Velocity		Temperature		Velocity	
	HA	TiO ₂	HA	TiO ₂	HA	TiO ₂	HA	TiO ₂
NPW	66780	273606	9218	9242	24	26	18	48
MGF	54348	168788	12306	3942	19	16	24	21
AGF	12303	58341	11541	869	4	5	23	5
CGF	14288	101426	988	759	5	10	2	4
RPM	6081	72167	131	1531	2	7	0	8
SPR	127871	375125	16429	2769	46	36	33	14

Easy-to-follow graphical representation of the relative PSP influence calculations could be seen from Fig. 5-8.

Fig. 5-8: Relative PSP influence

5.2.4.1 Hydroxyapatite

The *temperature* is influenced mostly by *spray distance* factor (45%), followed by *net power* (24%) and *main gas flow* (19%). Other factors do not make significant contribution to the changes in the temperature of HA particles. The in-flight *velocity* is influenced by a dominant *spray distance* factor (32%) and three equally impacting parameters: *main* (24%) and *auxiliary gases flows* (23%) and *net power* (18%). The results are in good accordance with the overall influence analysis carried out in 5.1.2 and the impacts of the factors determined by the Taguchi method correspond to the results obtained by OAAT method. Small differences in the influence of carrier gas flow factor (as compared with the theoretical 2x accrual recalculation, Table 37) are presumably caused by the impossibility to detect the peak-type dependence induced by the carrier gas effect.

5.2.4.2 Titanium dioxide

As well as for HA, the in-flight *temperature of TiO₂ powder* particles are mostly influenced by *spray distance* (36%), *net power* (26%) and *main gas flow* (16%) factors. *Net power* factor (48%) has the strongest influence on the *velocity of the particles*, followed by *main gas flow* (21%) and *spray distance* (14%) factors. The higher influence of the spray distance factor on the in-flight temperature as compared to net power factor does not correspond to the overall influence according to OAAT method where the influence of both factors was almost equal. However, the overall results are in good agreement with the previously obtained OAAT results.

The relative influence of the six PSP on the *temperature* of HA particles qualitatively matches the factors impacting the temperature of TiO₂ powder: dominant spray distance factor, followed by net power and main gas flow factors. The *difference in the relative impact of respective PSP* on the *in-flight velocity* of HA and TiO₂ powders could be caused by different mass density of the powders, as described in 5.1.1. While spray distance remains the most influencing factor for velocity of HA powder (followed by equally impacting main and auxiliary gases flows and net power factors), the most impacting factor on TiO₂ in-flight velocity is net power, followed by main gas flow.

Determined percentage distribution of particular PSP influence provides overview on the process of plasma deposition and aids to clarify the way the powder particles are influenced in the plasma jet. The knowledge was a crucial factor in determining the weight distribution of particular parameters in the process of theoretical description of the plasma spraying via governing equations (5.3.2).

5.3 Regression Analysis

The methodology and description of the regression analysis were given in 3.2.1.4.

The *influences of the six PSP* on temperature and velocity of HA and TiO₂ particles *were specified* in OAAT. The results of the 24 measurements were used for regression analysis in the first step. Four types of dependencies were considered and goodness of fit using correlation coefficient and standard error values was determined. To complete the theoretical description of the individual PSP on the process, unknown *coefficients of the selected dependencies were calculated*.

In the second step, *governing equations were constructed* to provide an overall description of the influence of all PSP on the measured characteristics. In this mathematical procedure, determined dependence types were used, supported by the results of the relative influence of the PSP and their mutual interactions according to the Taguchi method.

5.3.1 Dependence Type Determination

The *determined dependencies* could be seen from Table 41 as well as the respective correlation coefficients and standard errors. For lucidity, the values of the correlation coefficients and the standard error values are rounded to two decimal places.

Table 41: Dependence types of particular PSP

Parameter	Dependence type				Correlation coefficient				Standard error			
	Temperature		Velocity		Temperature		Velocity		Temperature		Velocity	
	HA	TiO ₂	HA	TiO ₂	HA	TiO ₂	HA	TiO ₂	HA	TiO ₂	HA	TiO ₂
NPW	Q	Q	Q	Q	0.94	1.00	1.00	1.00	4.70	10.09	3.47	2.23
MGF	Q	L	ME	L	1.00	1.00	0.96	0.99	2.74	5.71	7.97	1.75
AGF	L	L	Q	L	0.99	0.97	0.96	0.98	1.59	3.97	6.15	0.93
CGF	Q	Q	Q	Q	0.94	1.00	0.97	0.83	21.39	1.80	3.07	2.57
RPM	ME	L	Q	L	0.98	1.00	1.00	0.99	4.60	3.80	0.61	1.00
SPR	L	L	L	L	1.00	1.00	1.00	1.00	7.37	10.26	4.90	0.55

In the table, L denotes linear, Q quadratic and ME modified exponential dependence type. It could be seen the *most frequent dependencies are linear and quadratic* (11 occurrences each) and there are only two dependencies following the modified exponential fit.

The existence of peak-type relations for carrier gas flow influence measured by OAAT method (Fig. 5-1 and Fig. 5-2) was confirmed by regression analysis as all four dependencies were proven to follow quadratic trend. Quadratic behavior was also detected for all net power factor dependencies with high levels of goodness of fit (high correlation coefficients and low standard errors). Spray distance factor was determined as linear in all four cases (two powders x temperature, velocity), each having correlation coefficient of 1 (i.e. perfect fit). This fact corresponds with the idea of the independence of spray distance on other parameters as indicated by OAAT, Taguchi plotting and Taguchi factor interactions methods.

There were no significant differences in the analysis results between the used powders, i.e. the goodness of fit of the dependence type determination exhibited minor scattering equally for both powders. It must be noted the method is a statistical way of results processing and is therefore mathematically correct, however, the measured data intrinsically include measurement errors. The minor changes due to the errors could influence the decisive criterion.

The analysis of the dependence types allowed *determining the coefficients of respective equations*. As the calculations were solely based on OAAT method results, the equations describe influences of particular parameters on one of the measured in-flight characteristics without respect to the values of other parameters.

$$\begin{aligned}
 T_{HA} &= 2339.52 + 36.65NPW - 1.70NPW^2 & v_{HA} &= 138.15 + 7.67NPW + 0.25NPW^2 \\
 T_{HA} &= 2419.55 - 2.11MGF + 0.03MGF^2 & v_{HA} &= 160.30 + 1.20MGF \\
 T_{HA} &= 2390.01 + 0.65AGF & v_{HA} &= 220.09 + 0.93AGF \\
 T_{HA} &= 2064.55 + 108.11CGF - 5.56CGF^2 & v_{HA} &= 176.10 + 24.61CGF - 1.26CGF^2 \\
 T_{HA} &= 2444.61e^{\frac{0.04}{RPM}} & v_{HA} &= 295.90 - 7.03RPM \\
 T_{HA} &= 3032.36 - 4.81SPR & v_{HA} &= 483.96 - 1.87SPR
 \end{aligned} \tag{Eq. 12}$$

The terms T_{HA} and v_{HA} indicate temperature and velocity of HA particles, respectively. The notation for TiO_2 powder is analogous:

In-Flight Properties

$$T_{TiO_2} = 1578.37 + 95.06NPW - 2.52NPW^2$$
$$v_{TiO_2} = 80.36 + 13.17NPW - 0.24NPW^2$$
$$T_{TiO_2} = 2334.29e^{\frac{5.24}{MGF}}$$
$$v_{TiO_2} = 176.19 + 0.52MGF$$
$$T_{TiO_2} = 2448.12 + 1.48AGF - 0.02AGF^2$$
$$v_{TiO_2} = 212.90 + 0.19AGF$$
$$T_{TiO_2} = 2293.58 + 28.22CGF - 1.13CGF^2$$
$$v_{TiO_2} = 203.27 + 6.38CGF - 0.34CGF^2$$
$$T_{TiO_2} = 2646.38 - 85.11RPM + 9.57RPM^2$$
$$v_{TiO_2} = 251.51 - 8.32RPM$$
$$T_{TiO_2} = 2855.35 - 3.84SPR$$
$$v_{TiO_2} = 291.84 - 0.66MGF$$

Eq. 13

For *quadratic type dependencies*, it was possible to calculate the *extreme values of temperature or velocity* (minimum or maximum) as well as to determine respective values of the particular parameter pertaining to the extreme values (Table 42).

As could be seen from the table, majority of the quadratic dependencies have negative coefficient *c* (of the *cx²* term), i.e. they possess maximum value of the measured (calculated) parameter. The absolute magnitude of the coefficient *c* indicates relative strength of the quadratic dependence (the lower the coefficient, the closer the dependence to a linear type).

Table 42: Temperature and velocity extremes of quadratic PSP influence types

Powder	Parameter	In-flight characteristics	Calculated coefficients			Extreme type	PSP value [kW, scfh, 1]	Extreme value [K, ms ⁻¹]
			a	b	c			
HA	NPW	Temperature	2339.52	36.65	-1.70	max	10.8	2537
	NPW	Velocity	138.15	7.67	0.25	min	-15.4	79
	MGF	Temperature	2419.55	-2.11	0.03	min	41.4	2376
	CGF	Temperature	2064.55	108.11	-5.56	max	9.7	2590
	CGF	Velocity	176.10	24.61	-1.26	max	9.8	296
TiO ₂	NPW	Temperature	1578.37	95.06	-2.52	max	18.9	2474
	NPW	Velocity	80.36	13.17	-0.24	max	27.6	262
	AGF	Temperature	2448.12	1.48	-0.02	max	38.0	2476
	CGF	Temperature	2293.58	28.22	-1.13	max	12.4	2469
	CGF	Velocity	203.27	6.38	-0.34	max	9.4	233
	RPM	Temperature	2646.38	-85.11	9.57	min	4.5	2457

The maximum temperature of HA powder (approximately 2590 K) could be reached at a carrier gas level of 9.7 scfh. Slightly lower temperature should be reached at 10.8 kW level of net power. The calculated negative value of net power level to reach minimal velocity of HA

particles is a consequence of the mathematical processing; it does not refer to a real situation and therefore cannot be considered valid. Maximum velocity (approximately 296 ms^{-1}) should be reached at 9.8 scfh flow of carrier gas. This value is almost identical to the value for reaching maximum temperature and it is therefore considered as a critical point in terms of powder in-flight characteristics. For TiO_2 powder, all four PSP following quadratic trend allow reaching approximately similar maximum temperature (2457 – 2476 K): net power, auxiliary and carrier gases flow and hopper revolutions. The maximum velocity of TiO_2 particles (262 ms^{-1}) should be reached by setting net power to 27.6 kW. This value is beyond the system safety limits and therefore cannot be used. Contrary to HA powder, the value 9.4 scfh of carrier gas flow to reach the maximum velocity (233 ms^{-1}) does not match the value to reach the maximum temperature (12.4 scfh).

5.3.2 Governing Equations

The results of regression analysis describe influences of particular PSP on the temperatures and velocities of particles within the plasma jet, experimentally measured in section (5.1.1). To complete the theoretical model, improve its accuracy and describe the process involving all investigated PSP, results of the Taguchi design experimental work (5.2.2) were incorporated.

Governing equations were constructed as a combination of dependencies determined on the basis of OAAT method and calculated relative PSP influences and estimation of their mutual interactions derived from Taguchi method. Two equations describe the temperature and velocity of both powders, respectively with following general notation:

$$T, v_{HA/TiO_2} = \sum_{PSP} w_{PSP} f_{PSP}(\text{level}_{PSP}) + PSP_{int} \quad \text{Eq. 14}$$

where $f_{PSP}(\text{level}_{PSP})$ is the influence function of particular PSP at selected level and PSP_{int} is a sum of the correction terms due to PSP interactions. Initial relative weights of $w_{PSP} = 1/6$ for each parameter were replaced by their *respective weight factors* (the sum of the weight factors equals to 1). The difference between the temperatures or velocities as calculated based on particular PSP equations and based on the governing equation is a result of mathematical processing and characterizes the concurrence of the investigated PSP on the measured in-flight characteristics.

In-Flight Properties

The consequence of the *PSP interactions* is inaccuracy in determination of the expected value. The difference between the calculated values (particular PSP dependencies vs. governing dependencies) is then influenced and the accuracy of characterizing the concurrently acting PSP is lowered. To characterize this phenomenon, *modifications of the governing equations* were carried out. The weight factors of the interacting PSP were lowered by a coefficient equivalent to the strength of the discovered interaction. To compensate this decrease, additional terms of mean values (calculated as two-parametrical values at average PSP levels of two interacting factors) of the measured characteristics were added with respective weight factors. Frequently, one PSP exhibited interaction with more PSP. To involve this, the weight factor of this PSP was reduced in sequent steps, i.e. lowered by a factor characterizing interaction with other PSP and subsequently lowered again by a factor characterizing its interaction with another PSP, etc. The final weight factors of particular PSP could be seen from Table 43 (rounded to two decimal places).

Table 43: Weight factors of particular PSP, governing equations

Parameter	Weight factors [%]			
	Temperature		Velocity	
	HA	TiO ₂	HA	TiO ₂
NPW	11.62	18.77	18.21	43.52
MGF	11.57	5.40	24.31	18.57
AGF	0.64	3.34	18.24	3.32
CGF	0.43	5.41	1.25	2.57
RPM	0.36	1.78	0.21	5.77
SPR	45.40	35.74	32.46	14.49
Sum	70.02	70.44	94.68	88.24

The significance of spray distance factor originates in the primary dominance of the factor and nonexistence of interactions with other parameters. The maximum difference of the sum of original weight factors (equal to 100%) and the weight factors modified based on the detected interactions reached 30% (temperature of HA particles).

The considered interactions and the respective compensational terms values with their respective weight factors could be seen from Table 44 (numbers rounded to two decimal places).

In-Flight Properties

Table 44: Interaction terms and respective weight factors, governing equations

Temperature						Velocity					
HA			TiO ₂			HA			TiO ₂		
Interacting factors	Term value [K]	Weight factor [%]	Interacting factors	Term value [K]	Weight factor [%]	Interacting factors	Term value [ms ⁻¹]	Weight factor [%]	Interacting factors	Term value [ms ⁻¹]	Weight factor [%]
NPW-AGF	2480.13	7.29	NPW-MGF	2412.25	7.21	AGF-CGF	282.93	4.91	NPW-CGF	215.45	5.30
NPW-CGF	2561.79	7.59	NPW-RPM	2415.56	4.92	CGF-RPM	286.78	0.40	MGF-AGF	218.61	2.47
MGF-RPM	2437.85	8.32	MGF-CGF	2475.14	5.68				AGF-CGF	228.69	0.88
AGF-CGF	2502.56	2.79	MGF-RPM	2492.89	4.83				AGF-RPM	226.72	1.53
AGF-RPM	2448.66	1.84	AGF-RPM	2484.60	3.50				CGF-RPM	232.65	1.59
CGF-RPM	2530.32	2.15		2478.45	3.40						
Sum	29.98				29.55			5.31			11.77

The total sum of the modified PSP weight factors and the weight factors of the interaction terms equals to 1. The interaction terms were combined into absolute term (PSP_{int}) inclusive of the absolute terms in the particular PSP influences multiplied by its respective weight factor to retain simplicity of the *governing equations*:

$$\begin{aligned} T_{HA} &= 2699.96 + 4.26NPW - 0.24MGF + 0.46CGF - 2.18SPR \\ &\quad - 0.20NPW^2 + 0.02CGF^2 + 8.87e^{\frac{0.04}{RPM}} \\ v_{HA} &= 279.23 + 1.40NPW + 0.29MGF + 0.17AGF + 0.31CGF - 0.01RPM - 0.61SPR \\ &\quad + 0.05NPW^2 - 0.02CGF^2 \\ T_{TiO_2} &= 2294.88 + 17.84NPW + 0.05AGF + 1.53CGF - 1.52RPM - 1.37SPR \\ &\quad - 0.47NPW^2 + 0.06CGF^2 - 0.17RPM^2 + 126.12e^{\frac{5.24}{MGF}} \\ v_{TiO_2} &= 162.78 + 5.73NPW + 0.10MGF + 0.01AGF + 0.16CGF - 0.48RPM - 0.10SPR \\ &\quad - 0.10NPW^2 + 0.01CGF^2 \end{aligned} \tag{Eq. 15}$$

The notation of the temperature and velocity of HA and TiO₂ powders is identical to that used for single PSP equations. As the coefficients were rounded to two decimal places for lucidity, some PSP with coefficients < 0.005 are not displayed in the equations.

The calculated predictions of the in-flight characteristics of the powders with respect to all investigated PSP theoretically describe the process of plasma deposition. Minor differences between real values and theoretical prediction could be expected due to the intrinsic errors in measurements and complexity in determination of factor interactions.

5.4 Software Simulations

The in-flight characteristics were measured using two experimental approaches and their theoretical notation was derived. To offer alternative insight and complete the knowledge of the influence of the six investigated parameters on the temperature and velocity of HA and TiO₂ particles, *software simulations were performed*.

The simulations followed the Taguchi experimental design, i.e. 18 runs under selected levels of particular parameters.

The *mutual comparison of the results predicted by the software and the real values* measured by SprayWatch & Hi-Watch systems could be seen from Table 45 (rounded values).

Table 45: Software predictions of in-flight properties

Taguchi set	Temperature [K]				Velocity [ms ⁻¹]			
	HA		TiO ₂		HA		TiO ₂	
	Software prediction	Measured value	Software prediction	Measured value	Software prediction	Measured value	Software prediction	Measured value
01	2317	2524	2390	2727	134	175	138	151
02	2095	2495	2050	2277	174	188	187	141
03	1943	2475	1855	2125	208	203	224	137
04	2752	2361	2819	2600	143	160	147	146
05	2053	2470	2081	2444	187	275	193	174
06	1951	2589	1947	2388	220	264	233	196
07	2682	2437	2736	2617	180	214	185	159
08	1965	2350	2006	2449	217	236	221	193
09	2119	2500	2184	2592	201	243	207	193
10	2095	2540	2050	2267	174	175	187	134
11	1982	2453	2196	2212	146	171	165	127
12	1924	2724	2032	2373	208	248	215	176
13	2171	2370	2225	2381	167	172	170	150
14	1887	2633	1918	2830	206	287	211	201
15	2040	2514	2077	2344	188	204	192	173
16	2119	2451	2184	2593	201	244	207	176
17	2682	2415	2736	2560	180	199	185	174
18	1965	2428	2006	2362	217	229	221	194

Substantial differences were detected between the calculated and measured values of the in-flight properties. A distinct trend between the two values (e.g. a uniform shift of one set with

respect to the other set) was found: calculated temperatures exhibited a ~ 300 K shift towards lower values compared to experimental results. This fact indicates low level of the results reliability. There is only a limited consistency level in the results, i.e. higher values of software prediction corresponding to higher measured temperatures and accordingly for lower values. Measured and calculated velocities exhibited a minor scatter of the values.

As the reliability of the system (Appendix A) and measuring accuracy of SprayWatch & Hi-Watch systems (Appendix A) were identified as satisfactory, the discrepancy in the results is probably caused by the Jets&Poudres software. Four reasons could cause the observed differences, linked to the software limitations:

- the impossibility to simulate internal feeding of the powder, one of the major factors influencing the trajectory of the particle within the jet
- the influences of main and auxiliary gases flows in the laboratory experiment is suppressed in the software as only one combination could be used (70% Ar, 30% He)
- the insensitivity of the software to the properties of the powder
- single particle flight simulation, i.e. suppression of the influence of powder feeding (involving the carrier gas flow and hopper revolutions factors)

The particle trajectory within the jet is a crucial factor for its heat intake and momentum transfers (2.1.2.5). Due to steep gradients in the plasma jet, minor changes in the trajectory cause substantial differences in the process of heating (melting, boiling) and acceleration. This fact in conjunction with the omission of the influences of some parameters was probably the main reason of the failure of the software to simulate the process accurately.

CHAPTER 6: COATING PROPERTIES

Another major part of the experimental work within this study was devoted to *measurements of the properties of coatings* deposited by plasma and cold spray processes. Based on the results of the in-flight characteristics measurements, six sets of samples were prepared by plasma spraying for each of the powders. Similarly, six sample sets were deposited using cold spray technique (2.2.2).

Some *basic coatings characteristics* measurements were carried out and the *microstructure of the coatings* was investigated. Relative changes in *phase compositions* of the coatings were investigated with respect to the original powder feedstock and a *porosity of the coatings* was investigated using various methods. *Surface roughness* and *adhesion strength* of the coatings, two crucial properties influencing the acceptance of the implant in the human body, were measured and the respective *micro-hardness* of the coatings was assessed.

6.1 Basic Coating Characteristics

The details of the characterization techniques used to assess basic properties of both plasma sprayed (PS) and cold sprayed (CS) coatings were given in detail in 3.2.2.1.

The measurements of the *width of plasma spray at different spray distances* (Table 46) indicates a shift between the measured values of HA and TiO₂ powders (accuracy 0.5 mm). The sprayed bands of HA coatings are slightly broader than those of TiO₂. This difference is probably caused by different mass density of the powders: the lighter HA particles experience higher scattering in the jet, resulting in broader coating bands per pass of the plasma torch.

Table 46: Plasma sprayed coating band widths

Spray distance [mm]	Band width [mm]	
	HA	TiO ₂
50	15.0	12.0
65	17.0	14.5
80	18.0	16.0
95	19.5	17.5
110	20.0	18.5
125	21.0	20.0
140	25.0	20.5
155	27.0	21.5

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The measured values follow a linear trend in the coating band widths of both powders. The measured values were used for calibration and setting of the focus distance of SprayWatch system in order to capture the particles from the entire cross-section of the plasma jet (3.2.1.1) and to determine the height of the step of robotic arm for production of coatings with uniform thicknesses (based on the normal distribution assumption as described in 3.2.2).

Due to the scattering, the deposited bands of HA coating did not create sharp edges and their rim was rather gradual transition with decreasing amount of deposited coating. This fact resulted in complicated determination of the edges and band widths. TiO₂ coatings were geometrically distinct with sharp edges.

Initial colors of the powders were cyan or light blue (HA) and ochre or yellowish grey (TiO₂). After deposition, the colors changed and the resulting coatings turned whitish or light grey (HA) and dark grey or blackish (TiO₂).

The *thickness of the produced coatings* was assessed. A total of 16 combinations were sprayed (Table 21) and the resulting coating thickness per one pass was measured. Due to anticipated lower deposition efficiency of HA powder, the number of robotic arm passes was set to 20, while 10 passes were carried out for TiO₂ powder.

Table 47 shows the measured thicknesses per one pass of the robotic arm (average values of 3 measurements). In the table, feedrates 1 and 2 are combinations of CGF and RPM factors (15 scfh, 3 and 18 scfh, 2) and PSP sets 1 and 2 correspond to combinations of NPW, MGF and AGF (9 kW, 60 scfh, 20 scfh and 15 kW, 100 scfh, 60 scfh) as set in 3.2.2.1.

Table 47: Determination of the thickness per pass of plasma sprayed coatings

Powder	PSP set	Average thickness [µm/pass]			
		Distance 75 mm		Distance 125 mm	
		Feedrate 1	Feedrate 2	Feedrate 1	Feedrate 2
HA	1	29	15	16	9
	2	23	14	16	9
TiO ₂	1	46	33	32	19
	2	47	35	30	21

It could be seen the coating thickness per pass of both powders is substantially lower for longer spray distance. This could be caused by the fact that the same amount of powder is

deposited into broader bands at longer spray distance, resulting in thinner coatings. Also, the colder and slower particles at higher spray distances (the decreasing temperature and velocity of the particles was proven by both OAAT and the Taguchi methods) might not attach to the surface as well as hotter particle of inferior kinetic energies.

The differences in the coating thickness due to different powder feedrates well correspond to the conversion experiment carried out to determine the amount of powder entering the jet at different levels of CGF and RPM. According to the auxiliary experimental results (Appendix Table 3), feedrate 1 corresponds to 6.7 gmin^{-1} of HA powder ($15.3 \text{ gmin}^{-1} \text{ TiO}_2$), while feedrate 2 corresponds to 4.3 gmin^{-1} of HA powder (10.6 gmin^{-1} of TiO_2). The higher amount of powder entering the jet (feedrate 1) resulted in thicker coatings for both powders. The decrease in the TiO_2 powder feeding ($10.6/15.3 = 0.69$) well corresponds to the average decrease of the coating thicknesses of TiO_2 powder at the four combinations (0.69). In case of HA powder, the average decrease in the coating thickness due to different powder feedrate was slightly lower (0.56) than the decrease in the powder feeding ($4.3/6.7 = 0.64$). This leads to the idea of slightly lower efficiency of the deposition process than the expected values at higher feedrates. On the other hand, the numerical difference is not as significant and the differences could be attributed to measurement errors.

Based on the results of coatings thickness per pass measurements, it was decided to *produce the coating samples using 15 (HA) and 10 (TiO_2) passes* of the robotic arm (with the exceptions of samples where similar thickness was necessary, e.g. fatigue experiments).

Six sample sets were produced for each of the powders using plasma spray as well as six cold sprayed samples. Using various methods, the *thickness of the coatings was measured*.

Due to the limitations of the CS samples, the thickness measurements using micrometric and optical microscopy methods were carried out for plasma sprayed samples only as well as the software simulations. SEM observations were performed for both thermal processes. The description of the microscopic measurement methodology is provided in 3.2.2.1 as well as the micrometric measurements details. The principles of the software simulations are given in detail in 3.3.2.

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The thicknesses measured by micrometric and microscopy methods correspond and the relative differences in the sample thicknesses are similar for both measurements (Table 48).

Table 48: Plasma sprayed coatings thickness measurement

Measurement method	Coating thickness [μm]											
	HA						TiO ₂					
	PS-A	PS-B	PS-C	PS-D	PS-E	PS-F	PS-A	PS-B	PS-C	PS-D	PS-E	PS-F
Micrometric	515	429	608	770	794	373	126	761	863	563	126	746
Optical and SEM microscopy	448	330	510	679	753	362	130	768	841	517	82	750
Software simulation	2073	2620	3213	3153	2073	2073	3607	2890	5753	1796	2752	4260

The thicknesses predicted by software simulations are incomparable to the other values and the software apparently does not approximate the real situation well. As certain trends in the software predictions were found, an additional computation was carried out: the calculated values of coatings thicknesses were divided by a calculated ratio (this ratio was selected to match the thickness of the PS-A sample, Fig. 6-1). However, the trends in the software calculated thicknesses still do not follow the experimental results and the values provided by the software are therefore incorrect in both absolute and relative terms.

Fig. 6-1: Thicknesses of plasma sprayed coatings

The knowledge of the plasma sprayed sample thicknesses allowed determining the exact number of robotic arm passes for production of coatings with uniform thicknesses, necessary for adhesion testing and fatigue lives experiments.

Due to limitations in coating build-up, the *thicknesses of the cold sprayed samples* were determined by SEM method only. Table 49 summarizes the measured values for the respective six cold sprayed samples.

Table 49: Cold sprayed coatings thickness measurement

Measurement method	Coating thickness [µm]					
	CS-A	CS-B	CS-C	CS-D	CS-E	CS-F
Optical and SEM microscopy	18	21	10	10	-	28

The thicknesses of the CS-A and CS-B samples (HA powder on Ti-6Al-4V substrate) are similar despite different number of cold spray torch passes (5 for CS-A, 10 for CS-B). This result indicates the coating build-up process stopped at certain level, a phenomenon frequently observed for cold spray processes (as explained in 2.1.3). To confirm this idea, an additional experiment was carried out. The set CS-A was sprayed three times with different number of cold spray torch passes (1, 5 and 10 passes). It was discovered the thickness of the samples differs only slightly, substantially deviating from a linear dependence of resulting thickness vs. number of torch passes. Therefore it could be concluded that the resulting coating is formed by the first layer only with limited additional coating build-up. The small difference in CS-A and CS-B thicknesses therefore could be attributed to the different number of passes and the influence of the other factors (pressure of working gas, pressure gas temperature, pressure of feeder gas) could not be determined.

The inferior thicknesses of CS-C and CS-D samples are arguably caused by the glass substrate used. Subsequent microstructure observations (6.2) revealed the resulting coating was non-continuous and considerable part of the glass substrate was not covered. The thickness measured using SEM method is of the same magnitude as the theoretical thicknesses of deposited single splats (2.1.1). It is therefore likely the CS-C and CS-D combinations created only first layer of splats with no additional build-up: the incoming particles bounced off the glass substrate or the loosely connected splats deposited formerly.

This idea corresponds to the fact that the CS-E combination did not create any coating at all. Instead of bonding, the TiO₂ particles of high kinetic energies chipped away microscopic fragments of the glass substrate, as observed using SEM technique.

The reason for inferior bonding of HA and TiO₂ particles to the glass substrates as compared to Ti-6Al-4V alloy substrates could be the difference in the nature of the substrate materials. The glass substrate is brittle and the bonding with incoming particles is limited as bouncing of the particles and damage to the substrate via abrasion occurs frequently. The softer

metallic Ti-6Al-4V alloy readily undergoes severe plastic deformations upon impact of the particle and is therefore susceptible to coating formation.

The relative differences in bonding of HA and TiO₂ particles onto glass substrates could be caused by the different hardness of the materials. Hardness of the laboratory glass is indicated as 5.5 at Mohs scale and lies in-between the hardness of HA (5) and TiO₂ (6-6.5). When sprayed, the hard TiO₂ particles act as mere abrasives, damaging the substrate without leaving perceivable traces of coating. The softer HA particles have certain probability of bonding with the substrate. This bonding, however, is limited and continuous coatings could not be created.

The sample CS-F is TiO₂ coating on the Ti-6Al-4V metallic substrate. Analogous to samples CS-A, CS-B, it was discovered the coating build-up ended after the first pass of the cold spray torch and the successive passes did not influence the thickness significantly. The thickness of the sample produced by 5 nozzle passes is slightly higher than that of CS-A sample (HA powder) produced under the same number of passes. This fact would indicate a higher suitability of TiO₂ powder for deposition onto metallic alloy substrates.

6.2 Microstructure

Optical microscopy and SEM imaging were used to assess the microstructure of the produced coatings. The procedure of the sample processing and preparations, methodology of imaging and potential constraints are provided in 3.2.2.2.

Top-layer morphology was studied in order to obtain a basic idea on the roughness of the coatings, shape and morphology of the splats or the overall quality of the coating overlay. The *cross-sections* of the respective coatings provided information on the inner microstructure of the coatings (shape and morphology of the splats, network of micro-cracks, internal coating porosity, interface adherence of coatings to substrates, verification of the substrate grit blasting procedure uniformity, etc.) as well as more detailed specification of the top-layer relative roughness or thickness evaluation.

6.2.1 *Top-layer morphology*

Due to insufficient depth of focus, the *top-layer of the plasma sprayed coatings* was not studied using optical microscopy. The performed SEM analysis showed relative differences in the roughness of the coatings and varying splat shapes (splashing, morphology).

Various SEM magnifications were used to assess the roughness and splat morphology. For illustration, the relative differences under 250x magnification are displayed.

6.2.1.1 *Hydroxyapatite*

For HA powder (Fig. 6-2), the most sintered top-layer appears to emerge under PS-E combination: virtually the entire coating was melted and the splats coalesced into a block of coating. Low level of roughness was therefore expected. On contrary, PS-B combination gave rise to a coating formed of non-sintered splats: individual particles could be seen partially attached. PS-B sample also possess lower content of sharp splat edges as compared to other samples.

Fig. 6-2: Plasma sprayed HA coatings, top-layer morphology, SEM

PS-A sample exhibited increased intensity of splats cracking and lesser degree of particle melting. No significant differences were observed between PS-C, PS-D and PS-F samples.

6.2.1.2 *Titanium dioxide*

As compared to HA, the differences in splat spreading are less obvious (Fig. 6-3).

Fig. 6-3: Plasma sprayed TiO_2 coatings, top-layer morphology, SEM

Samples PS-E and PS-F exhibited high surface roughness where individual particles or splats were difficult to detect. Samples PS-C and PS-D showed average roughness with higher level of splat sintering. Individual, well molten and highly splashed splats were found in PS-B sample, indicating inferior level of the coating sintering. PS-A sample coating demonstrated proper melting, the level of splat sintering was comparable to that of PS-C and PS-D samples.

6.2.1.3 Cold sprayed samples

The *top-layer of the cold sprayed samples* was assessed using both optical and SEM microscopy.

The optical microscopy (Fig. 6-4) performed at lower magnifications confirmed the observations made in the thickness measurement section (6.1). CS-A and CS-B samples do not exhibit any major differences in terms of splat splashing and their respective surface roughness. The lower layer of splats (grey color) is covered with second layer of seemingly different properties (white color). The quality of the coating overlay is inferior to that of plasma sprayed samples as some substrate areas remained uncovered. The coating CS-A exhibited slightly lower level of substrate coverage than that of CS-B sample.

Fig. 6-4: Cold sprayed HA coatings, top-layer morphology, optical microscope

The coatings under CS-C and CS-D parameter combinations were deposited onto glass substrates, resulting in low coating overlay ratio. This is in accordance with the previously indicated non-continuity of the coatings, described in the thickness evaluation measurement (6.1).

The optical micrographs of CS-E sample confirmed non-existence of the coating as all particles bounced off the glass substrate, leaving grit-blasting marks on the surface. Additional

experiment was carried out to confirm this phenomenon: increased number of cold spray torch passes resulted in increased damage of the glass and, subsequently, a complete destruction of the substrate. The sample CS-F was not observed using optical microscopy.

The results of SEM imaging of the top-layer of the cold sprayed coatings (Fig. 6-5) corresponded with the optical microscope observations.

Fig. 6-5: Cold sprayed coatings, top-layer morphology, SEM, various magnifications

CS-A and CS-B samples display a two-layered structure. Some splats can be recognized in the bottom layer while there are no apparent splat boundaries in the top layer. SEM investigation of CS-C, CS-D samples revealed the nature of the ‘isolated splats’ observed by optical microscopy. The areas of coating on the glass substrate are, in fact, formed by a planar

coalescence of perfectly sintered splats. As the measured thickness of these objects approximately matches that of single deposited splats, the coalescence probably does not occur in perpendicular direction, i.e. there is no coating build-up by stacking of successive layers. The CS-D splats exhibited slightly inferior splashing. This could be caused by the increased deposition temperature of pressure gas and slightly increased pressures of working and feeder gases as compared to CS-C combination. The CS-F sample (displayed under two magnifications) exhibited superior overlay quality with no visible uncovered substrate areas. Particular splats with sharp edges structure were detected in the images. All cold sprayed samples exhibited approximately similar surface roughness.

As compared to plasma deposited layers, observation of the single splats is almost impossible for cold sprayed coatings. The structure of CS coatings appears to be composed of first layer of properly melted particles, overlapped by 'snowflakes' of successively deposited particles.

6.2.2 Cross-section observations

The sample cross-sections were prepared using a standardized procedure, described in 3.2.2.2. The plasma sprayed sample cross-sections were observed using both microscopy techniques while the cold sprayed samples were investigated using SEM imaging only.

6.2.2.1 Hydroxyapatite

The optical microscopy image of PS samples could be seen from Fig. 6-6. Some illustrative images of the coatings acquired by SEM technique could be seen from Fig. 6-7.

The sample PS-A is a well-sintered coating with low quantity of relatively short, mostly vertical micro-cracks. Single splats are difficult to be identified and the interface adherence to a substrate is sufficient. The pores are spherical in nature and the total porosity level is low. The sample PS-B exhibits a messy structure with easily identifiable splats, separated by connected voids. As the relative size of the void chains is big, the coating has a high level of total porosity. A small gap between the coating and the substrate could be seen as compared to PS-A sample. The PS-A and PS-B samples exhibit average roughness of their top-layers. PS-C coating contains considerable number of long vertical micro-cracks, frequently spanning through the entire coating width. The coating structure at the vicinity of the coating/substrate

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interface consists of particular splats separated by the typical void chains. The successive coating layers are, however, formed of well-sintered particles with the intrinsic spherical porosity (the porosity level is one of the highest among the HA coatings). The interface connection of the coating is perfect, with no visible gap between the coating and substrate. The roughness of the surface seems among the highest of the HA samples.

Fig. 6-6: Plasma sprayed HA coatings, cross-section features, optical microscope

The lamellar structure of the PS-D sample is clearly visible, surpassing that of sample PS-B. The single splats are easily visible and separated by the void chains. However, the overall porosity of the sample appears lower than samples PS-B and PS-C. Some long vertical cracks spanning the entire thickness could be seen in the coating. A network of both horizontal and

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vertical micro-cracks of medium lengths could be seen in PS-E sample. The coating is well-sintered with some medium-size spherical and occasionally big irregular pores. The overall porosity is estimated to be one of the lowest among the HA coatings. Both PS-E and PS-D samples possess average roughness of their surfaces. The messy structure of the PS-F sample contains easily recognizable single splats as well as the void chains. The average size of the chains appears bigger than that of sample PS-D. There are no prominent macro-cracks in the entire coating and its adherence to a substrate is good with all grit-blasting cavities filled with solidified particles. The roughness of the surface is lower than other HA coatings.

Fig. 6-7: Plasma sprayed HA coatings, cross-section features, SEM, various magnifications

6.2.2.2 *Titanium dioxide*

The optical microscopy images of TiO_2 PS samples could be seen from Fig. 6-8. Some illustrative images of the coatings as acquired by SEM technique could be seen from Fig. 6-9.

Fig. 6-8: Plasma sprayed TiO_2 coatings, cross-section features, optical microscope

One of the highest porosity levels was observed in the PS-A coating of inferior thickness. The porosity morphology is a transition between the spherical shape and the void chains. The adherence to a substrate is apparently low as there is a clear gap between the first deposited layer and the substrate along the entire interface. No micro-cracks were observed in the entire coating. A well-sintered structure of PS-B sample contains increased amount of relatively small pores, however, the total porosity is lower than that of PS-A. Big vertical cracks present

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in the coating are frequently connected by a horizontal crack approximately in the middle of the coating thickness. The horizontal cracks are ‘bridged over’ by occasional single splats. The small asperities of the substrate roughness are completely filled with the coating, higher adhesion strength is therefore expected.

Fig. 6-9: Plasma sprayed TiO_2 coatings, cross-section features, SEM, various magnifications

The sintered structure of PS-C contains a considerable amount of microscopic spherical pores as well as a dense network of distinctive vertical and horizontal cracks. The existence of the horizontal cracks could be explained by the short pause between the successive plasma torch passes, resulting in periodical heating and cooling of the topmost layers. Consequently, the adhesion of a deposited layer onto the previous layers could be affected, giving a rise to the

crack initiation. The adherence of the PS-C coating to a substrate is average, with some small voids present at the interface. The PS-D sample resembles the PS-C sample. The sintered structure contains a spherical porosity of a level similar to that of PS-C. However, as compared to PS-C, there are virtually no major cracks present and also the adherence to the substrate is superior. The thinnest PS-E sample exhibits the lowest porosity level of the TiO₂ coatings. The structure is well sintered, without any micro-cracks and its adherence to a substrate is high. The morphology of the PS-F sample cross-section resembles the PS-B sample. Relatively well sintered structure of the thick coating contains small voids and pores as well as some major cracks. The interface adherence of PS-F is good with some small gaps at the edge. In general, all TiO₂ coatings possess low roughness with no distinctive differences among the samples.

6.2.2.3 Cold sprayed coatings

The microstructure of *cold sprayed coatings* could be seen from Fig. 6-10. Due to the insufficient coverage of the CS-C and CS-D samples, illustrative images of CS-A, CS-B and CS-F samples only are displayed.

There are no distinct differences between CS-A and CS-B samples in terms of coating density, porosity or cracking. Both coatings are dense with virtually no cracks present. Higher magnifications (5000x) revealed microscopic network of pores within the coatings, however, the overall porosity level is low. The average roughness of both samples is similar. Distinct non-continuity was observed at the interface of cold sprayed coatings and a substrate. This indicates low adhesion of the produced coatings, contrary to the prediction (Table 1). The TiO₂ sample CS-F possesses lower porosity as compared with CS-A, CS-B samples and with no microscopic pores observed at high magnifications. Cracking of the CS-F coating does not occur. The roughness of the sample appears lower than that of CS-A, CS-B samples. All investigated samples were perfectly sintered and no individual splats could be distinguished from cross-section observations.

Additionally, the analysis of the acquired SEM images confirmed the uniformity of the grit-blasting process for all Ti-6Al-4V substrates.

Fig. 6-10: Cold sprayed coatings, cross-section features, SEM, various magnifications

6.3 Phase Composition

The composition of the deposited coatings was assessed using two methods. *X-ray diffraction spectra were collected* and subsequent analysis of the results provided information on the respective *phase composition of plasma sprayed and cold sprayed samples*. To assess the *element composition of the samples*, *energy-dispersive X-ray spectroscopy* was used.

6.3.1 X-Ray Diffraction

The process of collecting the spectra and subsequent procedure of Rietveld analysis of the collected data are given in detail in 3.2.2.3.

The *collected patterns* were compared to the patterns of the initial powder feedstock (HA, Fig. 4-1, TiO₂, Fig. 4-2) and the subsequent *Rietveld analysis* provided numerical estimation of the measured results and specified the relative phase changes in the coatings due to the plasma deposition.

6.3.1.1 *Hydroxyapatite*

For *plasma sprayed HA* coatings, the relative differences could be seen from Fig. 6-11. Some differences in the peak intensities could be observed as well as some extra peaks in the sample spectra belonging to other calcium phosphate phases, changes in the phase composition are therefore expected. The peak at 37.346° belongs to the detrimental CaO phase and was detected in all investigated coatings.

Fig. 6-11: XRD spectra of plasma sprayed HA samples

As the standard analysis of the acquired spectra is complicated due to high number of considered phases, the numerical analysis results provided more lucid view. The results of the analysis could be seen from Table 50 (results of initial powder feedstock analysis could be seen from Table 31).

It could be seen there are major changes in the phase composition, particularly in the content of the original HA phase in the samples. Of the original HA phase, the highest decrease

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occurred for PS-A sample (19% of HA remained). On contrary, almost 52% of HA phase was retained in PS-B sample.

Table 50: Rietveld analysis of plasma and cold sprayed HA samples

Phase	Phase content [%]										
	Powder	PS-A	PS-B	PS-C	PS-D	PS-E	PS-F	CS-A	CS-B	CS-C	CS-D
HA	92.79	18.62	51.77	41.02	33.35	39.29	28.58	98.44	98.98	100.00	100.00
α -CPP	0.71	3.94	1.87	0.00	0.00	0.21	18.82	0.00	0.00	traces	traces
β -CPP	Traces	0.00	11.34	0.00	0.00	0.00	16.83	0.00	0.00	traces	traces
Ca(OH) ₂	0.44	0.00	traces	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00
CaCO ₃	5.43	0.00	0.00	traces	traces	0.00	0.00	0.00	0.00	traces	traces
CaO	0.53	14.58	26.10	8.46	3.70	5.40	1.26	traces	traces	0.00	0.00
α -TCP	0.04	2.13	0.21	0.00	7.27	3.95	12.09	0.00	0.00	traces	traces
β -TCP	0.00	11.23	1.25	15.06	11.92	14.44	7.32	1.56	1.02	traces	traces
TTCP	0.06	49.51	7.47	35.45	43.76	36.70	14.62	0.00	0.00	traces	traces

The content of the detrimental CaO phase increased predominantly in the samples PS-A, PS-B. Substantial amount of TTCP phase emerged in all samples after the deposition, reaching almost 50% in PS-A sample. No CaCO₃ phase was detected in the samples and only traces of Ca(OH)₂ were present. The calcium pyrophosphate phases appeared mainly in the PS-F sample. β -TCP phase appeared in all investigated coatings, following the increase in TTCP phase content. The increase of its α -TCP phase was not as significant. Recrystallization of HA phase (2.1.1.2) presumably occurred for some samples (particularly PS-E) as the calculated preferred orientations of the crystallographic planes of hydroxyapatite within the sample were indicated as (0 2 1) and (0 0 4) as compared to initial (0 1 0) and (0 0 2).

6.3.1.2 Titanium dioxide

The collected XRD spectra of the *plasma sprayed TiO₂* coatings and comparison with the initial powder feedstock could be seen from Fig. 6-12. Some minor differences could be found in the measured spectra, however, the main peaks of rutile phase are preserved for all samples. The doublet of small peaks at 69.008° and 69.788° observed in all sample spectra belongs to rutile phase and was not detected in the initial powder feedstock. The small peak at 25.281° belongs to anatase phase and was observed for PS-A, PS-C, PS-E and PS-F samples.

Fig. 6-12: XRD spectra of plasma sprayed TiO₂ samples

Subsequent Rietveld analysis confirmed the idea of minor changes in the phase composition of the samples (Table 51; results of initial powder feedstock analysis can be seen from Table 32). As expected from the acquired spectra, small increase in the anatase phase content could be observed for the samples (particularly sample PS-A). Brookite phase remained virtually non-present in all measured spectra. The minor scattering in the values of hematite and quartz could be caused by measurement deviations. Recrystallization analysis for TiO₂ samples indicated (0 1 1) and (0 0 2) preferred orientations of the crystallographic planes of rutile phase in almost all samples (mainly PS-C, PS-D).

Table 51: Rietveld analysis of plasma and cold sprayed TiO₂ samples

Phase	Phase content [%]							
	Powder	PS-A	PS-B	PS-C	PS-D	PS-E	PS-F	CS-F
Rutile	90.90	87.19	97.77	96.35	98.37	94.21	94.83	99.49
Anatase	3.60	12.68	2.01	3.63	1.23	4.19	3.68	0.00
Brookite	traces	0	traces	traces	0.66	traces	0.06	0.50
Hematite	4.03	traces	traces	traces	traces	traces	1.37	traces
Quartz	1.47	0.12	0.23	0.02	0.07	1.59	0.06	0.00

6.3.1.3 Cold sprayed coatings

The acquired XRD spectra of *cold sprayed samples* could be seen from Fig. 6-13. There are no substantial changes in the measured spectra as compared to the initial powder feedstock for cold sprayed HA samples. The intensity of the peaks is constant, slight changes are expected in CS-A, CS-B samples due to presence of small peak at 41.088° pertaining to β -TCP phase. The spectra of the cold spray TiO_2 coating (CS-F) differ from the original TiO_2 feedstock in the intensities of the main peaks. However, no new peaks could be seen, indicating non-presence of other phases.

Fig. 6-13: XRD spectra of cold sprayed samples

The results of Rietveld analysis of cold sprayed spectra could be seen from Table 50 (HA) and Table 51 (TiO_2). The analysis confirmed the presumption of minor increase in β -TCP phase content in CS-A and CS-B samples. However, the increase was negligible and the dominant phase in the coating remains pure HA. No changes were numerically confirmed for CS-C, CS-D phases. Also TiO_2 CS-F coating did not exhibit any changes in the composition. No preferred crystallographic planes were detected in the measured spectra of both HA and TiO_2 cold sprayed samples.

6.3.2 Energy-Dispersive X-ray Spectroscopy

The sample preparation, methodology of measurement and the subsequent energy-dispersive X-ray spectra treatment were described in detail in 3.2.2.3.

The *calculated weight and atomic balances* of the coatings were compared to the element compositions of the initial feedstock (Table 33 for HA, Table 34 for TiO₂). The analysis of the measured HA spectra focused on the ratio of calcium to phosphorus (Ca/P), as an indicator of amount of other phases present in the sample. For TiO₂ coatings, the ratio Ti/O provided information on prospective oxidation of the particles during the thermal deposition processes.

6.3.2.1 Hydroxyapatite

Table 52 summarizes the results of the EDX spectra analysis for *HA* samples. The theoretical balance of Ca/P/O/H of crystalline HA is 39.89/18.50/41.41/0.20 wt%, i.e. the produced HA powder was almost pure. It could be seen there is a significant fall in the percentage content of both Ca, P while the content of oxygen increased for plasma sprayed samples. The differences are caused by a presence of other phases, as indicated by the changes in Ca/P ratio. While pure crystalline HA possess a ratio of 1.67, other phases have different Ca/P ratio values (TTCP 2.0, TCP 1.5, CPP 1.00; Table 9) and their presence therefore alters the ratio. The presence of detrimental CaO phase increases the Ca/P ratio.

Table 52: EDX spectra of plasma and cold sprayed HA samples

Element	Weight %										
	HA	PS-A	PS-B	PS-C	PS-D	PS-E	PS-F	CS-A	CS-B	CS-C	CS-D
Ca	40.95	30.26	30.30	37.95	31.22	34.54	30.52	14.93	18.46	15.87	14.43
P	18.87	11.74	14.70	14.49	15.09	15.07	15.63	10.57	11.94	11.06	10.93
O	40.18	58.00	55.00	47.57	53.68	50.39	53.85	74.49	69.60	73.08	74.65
	Atomic %										
	HA	PS-A	PS-B	PS-C	PS-D	PS-E	PS-F	CS-A	CS-B	CS-C	CS-D
Ca	24.67	15.87	16.28	21.63	16.88	19.18	16.48	6.95	8.88	7.45	6.70
P	14.71	7.97	10.21	10.69	10.55	10.81	10.92	6.37	7.43	6.72	6.56
O	60.62	76.16	73.51	67.68	72.56	70.01	72.6	86.68	83.69	85.84	86.74
Ca/P ratio	1.68	1.99	1.59	2.02	1.60	1.77	1.51	1.09	1.20	1.11	1.02

Samples with Ca/P ratio higher than that of pure HA are expected to contain a significant amount of TTCP or CaO phases. According to EDX analysis, the samples were PS-A, PS-C and PS-E. This result corresponds to the results of XRD analysis (TTCP content of 49.51%,

35.45% and 36.70%, respectively and CaO content of 14.58%, 8.46 and 5.40%, respectively). Samples with low Ca/P ratio are expected to contain CPP and TCP phases mainly. PS-F specimen has the lowest Ca/P ratio among the samples. Again, this was confirmed by the XRD analysis (highest levels of CPP and TCP phases). The samples with slightly lower Ca/P ratio (PS-B, PS-D) contain balanced amounts of TTCP, CaO, TCP and CPP phases. This is in accordance with the XRD analysis results (PS-B: 7.47% TTCP, 26.10% CaO, 13.21% CPP, 1.46% TCP; PS-D: 43.76% TTCP, 3.70% CaO, 19.19% TCP). It must be noted the measured element balances are influenced by the impossibility to detect hydrogen atoms (3.2.2.3), present in majority of the calcium phosphate phases.

6.3.2.2 *Titanium dioxide*

Table 53 summarizes the results of the element analysis for *TiO₂* samples. As could be seen, the changes in the titanium atoms content are not as significant for samples PS-A, PS-D, and PS-E, minor phase changes are therefore expected (the theoretical weight balance of Ti/O is 59.94/40.06). Samples PS-B and PS-C indicate different amount of *TiO₂*. The Ti/O atomic % ratio of the *plasma sprayed* samples exhibited scattering around the 0.49 ratio of the initial powder. The lower ratios (PS-A, PS-C, PS-D) indicate presence of oxidation and phase changes during the deposition process. The three samples were confirmed to contain anatase phase by the XRD method (12.68%, 3.63% and 1.23%, respectively). The samples with higher ratio (PS-B, PS-E, PS-F) were determined to contain the highest amounts of *SiO₂* (quartz) by the XRD analysis, which could partially explain the increase in the ratio. However, the content of the quartz phase was low and could not cause such Ti/O ratio increase. Further examinations will be needed to explain this phenomenon.

Table 53: EDX spectra of plasma and cold sprayed *TiO₂* samples

Element	Weight %							
	TiO ₂	PS-A	PS-B	PS-C	PS-D	PS-E	PS-F	CS-F
Ti	58.31	57.04	69.65	45.23	54.57	61.95	66.44	67.83
O	41.69	42.96	30.35	54.77	45.43	38.05	33.56	32.17
	Atomic %							
	Ti	O	Ti	O	Ti	O	Ti	O
Ti	32.72	30.76	43.42	21.62	28.65	35.28	39.84	43.27
O	67.28	69.24	56.58	78.38	71.35	64.72	60.16	56.73
Ti/O ratio	0.49	0.44	0.77	0.28	0.40	0.55	0.66	0.76

6.3.2.3 Cold sprayed coatings

Results of the element analysis of the *cold sprayed samples* could be seen from Table 52 for HA samples and Table 53 for the TiO₂ sample. The Ca/P ratios of the HA samples (CS-A 1.09, CS-B 1.20, CS-C 1.11 and CS-D 1.02) are similar, however, lower than the value of the powder feedstock (1.68). The decrease in the ratio indicates a presence of other phases (CPP or TCP). Small amount of β -TCP phase was detected by XRD analysis for CS-A, CS-B samples. The amount of the phase is, however, negligible and the drop in the Ca/P ratio due to the presence of this phase would be expected to be substantially lower. Furthermore, the samples CS-C, CS-D were indicated as pure HA by the XRD analysis, i.e. their Ca/P ratio should remain unaltered. The sample CS-F exhibited increased Ti/O ratio and was determined to contain a small amount of brookite phase by XRD method. However, the amount of brookite (0.50%) was insufficient to cause the drop in Ti/O ratio. In these cases, the results of the EDX analysis of the cold sprayed samples did not match the results obtained by the XRD method.

6.4 Porosity

For plasma spray technology, porosity levels of 2 - 20% are indicated in the literature (Table 1). To obtain unbiased information, various techniques were used to assess the *porosity of the produced plasma sprayed coatings*. Software analysis of SEM images of sample cross-sections and pycnometric methods provided information on the internal porosity levels and mercury intrusion porosimetry provided information on the open porosity. The details of the experimental procedures of three methods are given in 3.2.2.4. The internal porosity of the coatings was simulated using specialized software code (details provided in 3.3.2). Total porosity of coatings was also derived from the fatigue lives experimental results (details of the derivation of the total porosity from the fatigue lives experiments are provided in 3.2.3.1).

The porosity was not determined for cold sprayed samples due to various constraints (sample sizes too small for pycnometric and mercury intrusion porosimetry methods, insufficient average pore sizes for image analysis).

6.4.1.1 Hydroxyapatite

Summary of the measured *porosities for HA plasma deposited coatings* could be seen from Table 54.

Table 54: Porosity of plasma sprayed HA samples

Sample	Average porosity [%]			
	Internal			Open
	Image analysis	Pycnometric method	Simulent software	Mercury intrusion
HA	-	7.99 ± 0.03	-	-
PS-A	6.85 ± 1.20	9.44 ± 0.31	11.88	22.41 ± 2.71
PS-B	12.84 ± 3.11	12.84 ± 0.65	11.37	27.85 ± 1.66
PS-C	12.01 ± 0.51	9.50 ± 0.66	11.46	10.06 ± 1.53
PS-D	17.03 ± 3.72	8.82 ± 0.20	11.15	11.47 ± 3.21
PS-E	8.28 ± 2.39	10.70 ± 0.61	10.88	9.78 ± 2.07
PS-F	15.20 ± 0.56	9.11 ± 0.40	11.25	8.79 ± 1.38

The levels of the *internal porosity* determined by the *image analysis* indicated the highest internal porosity of sample PS-D (average in-flight temperature and velocity). The low and high extreme in-flight properties (samples PS-A, PS-F) led to low and high porosity, respectively. According to the kinetic energy and particle melting theory, opposite trend would be expected. The samples PS-B and PS-C possess similar porosity levels. Subsequent statistical analysis was performed in order to determine prospective inequality of the measured values. The standard deviations of the measurement sets were evaluated using F-test and the results were used in t-test results evaluation (3.2.2.4). It was discovered that the measured internal porosity levels of the samples are different from each other, i.e. the differences in the porosities are statistically significant. The hypothesis that the mean values of the average porosity sets are equal was rejected (at 95% confidence level) for four doublets: PS-A and PS-E, PS-B and PS-C, PS-B and PS-F, PS-D and PS-F. For these samples, the differences in the measured values were considered statistically insignificant.

The porosity levels measured by *pycnometric method* are based on the theoretical values of bulk density of HA (3.156 gcm^{-3} , 2.2.2.2). Results of the pycnometric experiments indicate similar porosity of all plasma sprayed HA samples with only minor relative differences. Sample PS-B (low velocity, high temperature) has slightly higher internal porosity (12.84%) than the other plasma sprayed samples. All the measured porosities are slightly higher than the porosity determined for the powder feedstock (7.99%), indicating the formation of internal porosity (spherical pores or void chains) in the coatings.

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The analysis of the *open porosity* of the coatings showed significant relative differences between the samples. The highest porosities of the low in-flight velocity PS-B, PS-A samples (27.85%, 22.41%, respectively) contrasted to the low open porosities of the high in-flight velocities of PS-F, PS-E (8.79%, 9.78%, respectively) samples. This is in accordance with general principles of the thermal deposition: higher kinetic energies give rise to coatings of inferior porosities. Medium porosity was measured for PS-C and PS-D samples in accordance with the theory.

The *internal porosity* level as calculated using Simulent Coat software code did not show significant differences between the coatings. The relative changes in the porosity of the samples are negligible and no conclusion on the influence of PSP can be made.

A *total porosity* of other HA coatings was calculated from *the results of fatigue lives experiments* (3.2.3.1). Density of three sets of HA coatings (not following the Taguchi sets) was calculated. The total porosity of the samples was obtained by comparing the density with theoretical values. The PSP configuration for spraying of the respective sets (denoted as HA-1 to HA-3) could be seen from Table 22.

The calculated total porosity of the samples could be seen from Table 55. The in-flight characteristics in the table are duplicated from Table 23. As could be seen, substantial differences were detected in the coatings. The highest porosity level (46.45%) corresponds to average in-flight temperature and velocity of the powder particles. The lowest porosity was obtained for the highest temperature and highest velocity, in accordance with general theory. It is necessary to note that the measurement of the total porosity of HA coatings using this method implicitly includes errors due to inaccuracy in determination of the coating thickness.

Table 55: Total porosity of plasma sprayed HA specimens for fatigue live experiments

Sample	In-flight properties		Calculated density [gcm ⁻³]	Total porosity [%]
	Temperature [K]	Velocity [ms ⁻¹]		
HA-1	2352	199	2.32	26.49
HA-2	2160	150	1.69	46.45
HA-3	1778	132	2.05	35.04

The *mutual comparison of the porosities assessed by different methods* is limited as different porosities were measured (open, internal). The total porosity, however, should

comprise both values. A graphical depiction of the measured values represents the most convenient way for the comparison (Fig. 6-14). As the PSP sets for fatigue lives experiments were different from the PSP sets of the six samples produced according to the Taguchi method results, the three sets were assigned to samples of the closest in-flight properties (HA-1 to PS-D, HA-2 to PS-B and HA-3 to PS-A) in the chart.

Fig. 6-14: Porosity of plasma sprayed HA samples

It was found that the image analysis and the pycnometric methods provide relatively similar results of the internal coating porosity (some differences were observed for PS-D and PS-F samples). The measured internal porosity values corresponded with the SEM porosity observations carried out in 6.2.2. The open porosity measured by mercury intrusion method does not follow the trend in the internal porosity measured by image analysis and pycnometric method. The total porosities determined from the fatigue lives experiments are in good agreement with the sum of levels of the open and internal porosities of PS-A, PS-B and PS-D samples. The small deviations in the total porosity and the sum of internal and open porosity could be caused by the fact the in-flight temperatures and velocities differed slightly for production of PS-A, PS-B, PS-D samples and HA-1, HA-2, HA-3 sets. The internal porosity

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calculated in the software simulations approximately matched the porosity as determined by pycnometric method. However, the small deviations in the pycnometric measurements were not observed for the results provided by the computer simulations.

The mercury intrusion porosimetry and SEM image analysis methods allowed *specification of the average pore sizes*. Using the detection ranges for locating the porosity within the SEM images, the software calculated average areas of the detected pores (Table 56). From the results, average pore diameter was subsequently calculated assuming circular geometry of the pores (such geometrical approximation may not be correct in case of void chains observed for some coatings). The measurement of the porosity using mercury intrusion method provided data on the average size of the open pores.

Table 56: Average pore sizes of plasma sprayed HA coatings

Porosity type	Parameter	Unit	PS-A	PS-B	PS-C	PS-D	PS-E	PS-F
Internal	Pore area	μm ²	8.84	4.91	5.82	7.9	8.43	5.03
	Pore diameter	μm	3.36	2.50	2.72	3.17	3.28	2.53
Open	Pore diameter	μm	0.06	0.09	0.03	0.02	0.02	0.03

There are only minor differences in the *internal pore diameters of the plasma sprayed HA samples*. A small difference in pore diameters could be detected for PS-A (3.36 μm), PS-E (3.28 μm) and PS-B (2.50 μm). Microstructure analysis of the samples indicated well-sintered structures of PS-A and PS-E samples with spherical porosity while chains of voids can be located in PS-B coating. As the PS-A, PS-E samples possess the lowest total porosity levels of HA coatings, the calculated big pore diameters lead to the idea of low density of the pores, which was confirmed by SEM investigations.

Open porosity assessed by mercury intrusion method showed some differences in the *average open pores sizes* (PS-B 0.09 μm, PS-D 0.02 μm). The literature views on the optimal pore size for successful bone in-growth vary (2.2.1.2), however, the measured values of the open pore diameters of the produced HA coatings appear undersized for such application.

6.4.1.2 Titanium dioxide

Summary of the *measured porosities for TiO₂ plasma deposited coatings* could be seen from Table 57.

Table 57: Porosity of plasma sprayed TiO₂ samples

Sample	Average porosity [%]			
	Internal			Open
	Image analysis	Pycnometric method	Simulent software	Mercury intrusion
TiO ₂	-	13.62 ± 0.64	-	-
PS-A	27.66 ± 6.17	24.70 ± 1.13	14.31	14.03 ± 2.41
PS-B	26.16 ± 3.76	22.31 ± 0.84	14.75	7.01 ± 3.52
PS-C	8.26 ± 1.51	25.61 ± 0.59	13.51	6.08 ± 1.64
PS-D	9.23 ± 1.26	22.26 ± 0.64	14.69	12.13 ± 2.64
PS-E	8.34 ± 1.83	20.39 ± 0.28	14.38	11.16 ± 3.64
PS-F	18.77 ± 0.87	22.81 ± 0.79	12.77	7.00 ± 1.07

Samples PS-A, PS-B indicated high levels of *internal porosity* as measured by *image analysis method*. The samples were deposited at low velocities and the high porosity is in accordance with the theory. There were no significant differences in the porosity of PS-C and PS-D samples, in agreement with their similar in-flight properties during the deposition process. As well as for HA coatings, the high-temperature high-velocity PS-F sample possess increased porosity as compared to its average counterparts (PS-C, PS-D). The statistical analysis (F-test, t-test, 95% confidence level) indicated that the mean values of the porosity are equal for (PS-A, PS-B) doublet and (PS-C, PS-D, PS-E) coating triplet. The variations of average porosity values of these samples were statistically insignificant.

The porosity of the samples measured by *pycnometric method* is based on comparison with the theoretical values of bulk TiO₂ (4.250 gcm⁻³, 2.2.2.3). Results show that there are only minor differences in the measured porosities. Samples PS-C (25.61%) and PS-A (24.70%) exhibit increased porosity, in accordance with the low velocity of particles during their deposition. PS-E sample exhibited the lowest porosity as measured by pycnometric method and samples PS-B, PS-D and PS-F demonstrate equivalent levels of internal porosity. The differences between the samples are, however, small and no conclusions can be made. The porosities of the six plasma sprayed samples were found to be substantially higher than the initial powder feedstock (13.62%).

The *mercury intrusion porosimetry* revealed the highest *open porosity* of the low temperature, low velocity PS-A sample (14.03%). The high temperature high velocity sample

PS-F exhibited, on contrary, the lowest level of open porosity (7.00%). Porosities of both samples therefore correspond to the theory. Slightly increased porosity of PS-D (12.13%) and PS-E (11.16%) samples as compared to PS-B (7.01%) and PS-C (6.08%) samples cannot be explained using this theory.

As well as for HA coatings, the *computer modeling* of the deposition process did not provide reliable data. The calculated porosities are similar and the influence of PSP on the porosity of the coatings cannot be determined by this method.

The *fatigue lives* experimental specimens were used for *evaluation of the total porosity* of the selected plasma sprayed samples. The calculated densities of three TiO₂ coatings (denoted as TiO₂-1 to TiO₂-3) necessary for porosity evaluation could be seen from Table 58. The measured in-flight characteristics are duplicated from Table 23 and the settings of the PSP for coating preparations could be seen from Table 22.

Table 58: Total porosity of plasma sprayed TiO₂ specimens for fatigue live experiments

Sample	In-flight properties		Calculated density [gcm ⁻³]	Total porosity [%]
	Temperature [K]	Velocity [ms ⁻¹]		
TiO ₂ -1	2385	197	3.75	11.76
TiO ₂ -2	2267	167	3.68	13.41
TiO ₂ -3	2168	128	3.54	16.71

The differences in the calculated sample porosities are small. However, the total porosity of the samples conforms to the in-flight temperatures and velocities measured for the samples: the higher the temperature and velocity of TiO₂ particles, the lower the overall porosity content.

Mutual comparison of the porosities measured by various methods could be facilitated using graphical plot of the measured data (Fig. 6-15). Analogous to HA sets, the three TiO₂ fatigue lives specimens were assigned to the corresponding coatings plasma deposited according to the Taguchi design (TiO₂-1 to PS-E, TiO₂-2 to PS-C, TiO₂-3 to PS-A).

Contrary to HA coatings, it was found that the internal porosity values provided by SEM image analysis method and pycnometric measurements differ substantially (e.g. PS-C, PS-D). The porosity levels measured by image analysis confirmed the cross-section observations in the process of microstructure evaluation (6.2.2).

Fig. 6-15: Porosity of plasma sprayed TiO₂ samples

The open porosity, assessed by mercury intrusion method, partially follows the trend observed by image analysis method. The absolute values are different, though, as both method measured different porosity types (open vs. internal). The total macroscopic porosity determined from the fatigue lives testing retained values similar to the computer simulated deposition process. Their absolute values were, however, inaccurate and did not comprise the sum of internal and open porosity, as in the case of HA coatings. The main reason for this fact could be bigger difference between the in-flight properties of TiO₂ particles for preparation of fatigue lives specimens and in-flight properties of the matching samples than in the case of their respective HA counterparts. The porosity evaluated using the software code remained virtually intact to changes in PSP and did not follow any measurement trends for TiO₂ coatings.

As well as for HA coatings, determination of the *average pore sizes of TiO₂ coatings* was carried out using mercury intrusion porosimetry and analysis of the SEM images. Selected detection ranges for locating the porosity within the SEM images were used and the software calculated average areas of the detected pores, as could be seen from Table 59. Under

simplifying assumption of circular geometry of the pores, the average pore diameter was then calculated. The measurement of the porosity using mercury intrusion method provided data on the average size of the open pores.

Table 59: Average pore sizes of plasma sprayed TiO₂ coatings

Porosity type	Parameter	Unit	PS-A	PS-B	PS-C	PS-D	PS-E	PS-F
Internal	Pore area	μm ²	9.78	10.68	4.22	7.15	6.79	4.82
	Pore diameter	μm	3.53	3.69	2.32	3.02	2.94	2.48
Open	Pore diameter	μm	0.03	0.01	0.02	0.02	0.02	0.01

It could be seen that there are differences in the average *internal pore sizes* among the TiO₂ coatings. However, such changes are not distinct. As well as for HA coatings, the well-sintered coatings (PS-A, PS-B) contain pores of biggest diameters while the average pore sizes of the messy splats structures (PS-C, PS-F) are deemed to have the smallest pore sizes.

The porosity measured using mercury intrusion method indicated no differences in the average *diameters of open pores*. The relative changes between the coatings are negligible and the suitability of the produced coatings for bone tissue-in growth in terms of average pore sizes is disputable.

The literature indicated the optimal porosity of the coatings within the 5 - 20% range (2.2.1.2). Lower porosity could restrict bone remodeling while higher porosity content could deteriorate the mechanical properties of the coatings. It was discovered the porosity of the produced coatings fall within the specified range.

6.5 Surface Roughness

The experimental setup for *surface roughness* measurements was provided in 3.2.2.5 as well as the description of the five measured profile roughness indicators.

To minimize the influence of random errors, the roughness of plasma and cold sprayed samples was *measured using a standardized procedure*. *Software simulations* of the plasma deposition process were carried out, offering values of average coating roughness as an alternative approach to the measurement.

6.5.1.1 Hydroxyapatite

The *results of the roughness measurements and software simulations for HA coatings* could be seen from Table 60.

Table 60: Roughness of plasma and cold sprayed HA coatings

Sample	Measured roughness [μm]					Software calculated roughness [μm]
	R_a	R_q	R_p	R_v	R_y	
PS-A	11.30	14.86	46.91	25.67	72.58	6.74
PS-B	9.80	12.37	33.10	29.44	62.54	11.27
PS-C	19.39	23.76	61.93	37.08	99.01	12.09
PS-D	12.43	15.69	43.25	28.32	71.57	10.33
PS-E	13.89	17.17	44.82	30.40	75.22	6.74
PS-F	7.41	9.36	28.96	21.16	50.12	3.42
CS-A	2.98	3.86	11.82	11.02	22.84	-
CS-B	3.23	4.27	15.32	10.55	25.87	-
CS-C	1.34	1.76	7.18	2.80	9.97	-
CS-D	1.33	1.65	5.20	2.46	7.66	-

The results indicate relative differences in the roughness of HA plasma sprayed coatings. High in-flight temperature samples (PS-B, PS-F) retained the lowest roughness levels among the HA samples (9.80 μm , 7.41 μm) while low and average in-flight temperature samples possessed higher roughness. Presumably, the high deposition temperature results in better particle melting, resulting in lower roughness levels. The highest surface roughness was exhibited by PS-C sample (19.39 μm). The measured roughness of HA coatings is in accordance with the SEM cross-section estimations carried out in 6.2.2.

The values of roughness of plasma sprayed HA coating were estimated using software simulations. The calculated values are shifted with respect to the values obtained using mechanical measurement, however, the trend in roughness variations with respective HA sample coatings was approximately followed by both methods. Again, the lowest roughness was calculated for PS-F sample (3.42 μm). The PS-C sample exhibited the highest surface roughness (12.09 μm), in agreement with the mechanical testing.

6.5.1.2 Titanium dioxide

The results of the roughness measurement and software simulations for TiO_2 coatings could be seen from Table 61.

The roughness of the plasma deposited TiO_2 coatings did not show substantial differences and the relative changes in the observed quantity are negligible. Apparently, the in-flight

properties did not significantly influence the roughness of the coating surfaces. The uniform roughness of the entire set ($\sim 5\text{ }\mu\text{m}$) is confirmed by similar values of the samples in R_v statistics (maximum height of the profile). This measurement corresponded with the observations made in the microstructure assessment (6.2.2).

Table 61: Roughness of plasma and cold sprayed TiO_2 coatings

Sample	Measured roughness [μm]					Software calculated roughness [μm]
	R_a	R_q	R_p	R_v	R_y	
PS-A	5.67	7.07	18.89	18.55	37.44	11.15
PS-B	4.80	5.97	16.01	16.32	32.33	14.46
PS-C	5.21	6.59	20.67	16.37	37.03	13.02
PS-D	5.72	7.15	20.53	18.11	38.64	11.85
PS-E	5.31	6.62	17.94	17.30	35.24	4.85
PS-F	7.15	9.04	27.38	19.78	47.16	10.54
CS-F	2.12	2.62	7.00	7.74	14.74	-

The values provided by the software showed considerable differences in roughness of TiO_2 coatings. No distinct trend in the roughness bound to the in-flight properties could be observed. The *roughness as calculated by the software code* has higher values as *compared to the data obtained by mechanical testing*. The lowest value for PS-E sample ($4.85\text{ }\mu\text{m}$, low in-flight temperature, high in-flight velocity) contrasts to the highest calculated roughness of PS-B sample ($14.46\text{ }\mu\text{m}$, high deposition temperature, low velocity).

6.5.1.3 Cold sprayed coatings

The *roughness of cold sprayed samples* could be seen from Table 60 for HA coatings and Table 61 for TiO_2 coating. It could be seen the samples deposited onto glass substrates (CS-C, CS-D) possess lower roughness ($1.34\text{ }\mu\text{m}$, $1.33\text{ }\mu\text{m}$) as compared to the combinations deposited onto Ti-6Al-4V alloy. There were not significant differences between the CS-A and CS-B samples ($2.98\text{ }\mu\text{m}$ vs. $3.23\text{ }\mu\text{m}$) as well as CS-C, CS-D, i.e. the cold spray parameters (CSP) did not influence the final roughness significantly. In accordance with the results for plasma sprayed coatings, the roughness of TiO_2 coating exhibited value lower (CS-F $2.12\text{ }\mu\text{m}$) than that of HA coatings.

6.6 Adhesion Strength

Detailed description of the sample preparation, testing procedure and the requirements of the ASTM-C633 standard for *adhesion strength testing* of plasma deposited are provided in section 3.2.2.6.

Theoretical values of bond strength of plasma sprayed coatings are within 10 – 70 MPa (Table 1). The values are surpassed by using cold spray technology. However, the insufficient thickness of produced CS coatings disallowed testing of their adhesion to substrates (ASTM standard requires at least 380 μm thickness). The adhesion testing was therefore carried out for plasma sprayed coatings only.

Table 62 shows the *measured adhesion strengths of HA and TiO₂ plasma sprayed coatings*. As the coating adhesion is significantly influenced by the thickness of the coating (2.1.3), the deposition parameters (robotic arm movement velocity, number of passes) were set to produce coatings of uniform thickness so as to eliminate the influence of the factor. The results of the coating thickness per pass measurement (6.1) were also used. The resulting coatings thicknesses are included in Table 62. All produced coatings conformed to the requirements of the ASTM standard.

Table 62: Adhesion strength of plasma sprayed coatings

Powder	Adhesion strength [MPa]		Coating thickness [μm]	
	HA	TiO ₂	HA	TiO ₂
PS-A	2.87	4.39	442	419
PS-B	0.68	4.23	455	421
PS-C	6.16	5.12	433	382
PS-D	3.38	6.17	498	461
PS-E	2.52	10.95	418	434
PS-F	1.61	7.58	488	457

The graphical representation of the adhesion strength values is provided in Fig. 6-16.

6.6.1.1 Hydroxyapatite

The PS-C sample exhibited the highest adhesion strength (6.16 MPa) of the *HA coatings*. On contrary, sample PS-B showed almost zero adherence to the substrate. To confirm the value, the adhesion strengths of PS-B set were measured repeatedly. The series exhibited the

lowest number of omitted experiments due to non-standard coating peel-off during the testing. The other samples possess approximately similar levels of adhesion with little differences. In general, the measured values are substantially lower than the values indicated in the literature. To clarify this discrepancy, further investigations would be needed.

6.6.1.2 *Titanium dioxide*

For TiO_2 powder, the low in-flight velocity samples (PS-A, PS-B) exhibited substantially lower values of adhesion strength (4.39 MPa, 4.23 MPa) than their high-temperature high-velocity PS-E, PS-F counterparts (10.95 MPa, 7.85 MPa). This is in accordance with the kinetic energy theory. This idea was furthermore confirmed: the samples produced under average in-flight characteristics (PS-C, PS-D), exhibited average levels of adhesion strength (5.12 MPa, 6.17 MPa).

Fig. 6-16: Adhesion strength of plasma sprayed coatings

The specimens from PS-F set cracked in the middle of the coating frequently. This is in accordance with the major cracks observed in the PS-F coatings using SEM technique (6.2.2). The adhesion strengths of the sets matched the SEM investigation predictions: the coatings

with small gaps between the coating and substrate exhibited lower adhesion strengths while samples with the substrate roughness asperities completely filled with coating possessed high levels of adhesion (6.2.2).

6.7 Micro-hardness and Elastic Modulus

The specifications of the hardness tester, methodology of *hardness measurement* and respective details are given in 3.2.2.7.

Due to various limitations, the two quantities describing the physical properties of the deposited coatings were measured for plasma sprayed samples only. The initial idea of measuring the properties using the cross-section samples was not realized due to inaccuracy in indentation targeting and the micro-hardness and elastic modulus were measured perpendicularly to the coating surface.

6.7.1 *Micro-hardness*

Micro-hardness of HA and TiO₂ plasma deposited coatings was assessed. Ten indentations were carried out per sample, each consisting of five loading and unloading cycles under increasing force (3.2.2.7).

Average values of the ten indentations were considered as the measured hardness of the sample. The results could be seen from Table 63.

Table 63: *Micro-hardness of plasma sprayed coatings*

Powder	Micro-hardness [GPa]	
	HA	TiO ₂
PS-A	1.16	0.40
PS-B	0.86	0.23
PS-C	0.06	0.73
PS-D	0.30	0.58
PS-E	0.26	0.29
PS-F	0.24	0.16

It could be seen that the measured levels of micro-hardness are lower than the values usually indicated for plasma sprayed ceramic coatings. However, as hardness is not a fundamental material property, its measured value depends on the setting of test parameters (applied force, etc.) and the absolute values could differ significantly. Furthermore, the values

could be influenced by the experimental setup (perpendicular micro-hardness testing, i.e. indentation into the surface of the coatings).

The method focused on measuring of the *relative differences in micro-hardness* of the investigated coatings. Graphical presentation of the relative differences is more lucid (Fig. 6-17). The samples deposited under high-velocities (PS-E, PS-F) exhibit the lowest levels of material hardness for both powders (HA: 0.26 GPa, 0.24 GPa and TiO₂: 0.29 GPa, 0.16 GPa).

For *HA* powder, the average in-flight characteristics resulted in coatings (PS-C, PS-D) of inferior hardness while low in-flight velocity induced highest hardness levels among the investigated HA set (PS-A 1.16 GPa, PS-B 0.86 GPa).

For *TiO₂* coatings, different situation occurred: the hardness level of PS-A, PS-B samples (0.40 GPa, 0.23 GPa) is comparable with the high in-flight velocity coatings (PS-E, PS-F) and the highest coating hardness was observed for samples PS-C (0.73 GPa), PS-D (0.58 GPa), related to average values of in-flight temperature and velocity.

Fig. 6-17: Micro-hardness of plasma sprayed coatings

Average hardness values of HA (0.48 GPa) and TiO₂ (0.40 GPa) sets do not differ significantly and (except for the PS-E, PS-F samples) there was no similar trend observed for the coatings.

6.7.2 Elastic Modulus

Elastic modulus of HA and TiO₂ plasma deposited coatings was determined using two methods: micro-hardness indentation method provided data on the elastic moduli of the coatings and the values were also calculated from the results of fatigue lives experiments (under simplifying assumptions).

The settings of the elastic module measurements using indentation method are identical with the setup for micro-hardness measurement and are described in 3.2.2.7. The details of the derivation of elastic moduli from the measured data are provided in 3.2.3.1.

The moduli measured by the indentation method (PS-A to PS-F) are results of microscopic pressure loading while the moduli derived from fatigue lives experiments (HA-1 to HA-3 and TiO₂-1 to TiO₂-3) are average values of elastic moduli in tension and compression. The measured values could be seen from Table 64.

Table 64: Elastic moduli of plasma sprayed coatings

Set	Elastic modulus [GPa]		Set	Elastic modulus [GPa]	
	HA	TiO ₂		HA	TiO ₂
PS-A	35.45	42.15	HA-1	14.27	
PS-B	26.82	36.58	HA-2	13.78	
PS-C	12.81	69.89	HA-3	13.99	
PS-D	17.29	32.34	TiO ₂ -1		78.45
PS-E	18.39	38.28	TiO ₂ -2		66.03
PS-F	20.29	35.36	TiO ₂ -3		56.79

Two samples exhibited increased values of elastic modulus among HA coatings. The values of 35.45 GPa and 26.82 GPa for PS-A and PS-B samples, respectively, are slightly higher than the other HA coatings. Samples PS-D to PS-F have approximately similar elastic moduli (~ 17 - 20 GPa) and the lowest modulus was detected for sample PS-C.

Contrary to HA, PS-C sample of TiO₂ coatings demonstrated the highest elastic modulus among the investigated set (69.89 GPa). PS-A sample exhibited slightly higher value (42.15 GPa) and the measured moduli of the other coatings were almost equal (~ 32 – 38 GPa).

The elastic moduli of coatings determined from the fatigue lives experimental work were significantly different for TiO₂ powder. For HA powder, the relative differences in the measured values are negligible and the coating sets have similar elastic moduli. Based on the

results of the in-flight characteristics measurements (Table 23), the fatigue lives specimens were associated with respective plasma sprayed sets according to the Taguchi method, analogous procedure as for the porosity measurements (6.4). Graphical representation shows the fatigue lives specimens displayed next to the corresponding PS sets (Fig. 6-18).

Fig. 6-18: Elastic moduli of plasma sprayed coatings

For *HA* coatings, the elastic modulus of PS-D sample matched the value obtained by fatigue lives experiments (17.29 GPa vs. 14.27 GPa). The other two samples (PS-A, PS-B) exhibited substantially higher values and no correlation of the values was found.

For *TiO₂* coatings, the measurements of elastic moduli were consistent and the results provided by both methods indicated similar values for PS-A and PS-C samples. The value determined for PS-E sample (78.45 GPa) did not match the modulus as measured by indentation method.

Mutual *comparison of the elastic moduli* of coatings deposited using *both powders* measurement indicated similar measured values for PS-A, PS-B samples. For other sample sets, *TiO₂ coatings exhibited superior elastic moduli* as compared to HA coatings (approximately 2x higher).