Characterization of plasma sprayed deposits : influence of process parameters

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Characterization of Plasma Sprayed Deposits: Influence of Process Parameters

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	3
TABLE OF CONTENTS.....	4
ABSTRACT.....	7
1. INTRODUCTION.....	10
1.1 Rationale.....	11
1.2 Objectives.....	14
1.3 Scope.....	15
2. LITERATURE REVIEW.....	18
2.1 Thermal spray technology.....	18
2.2 Thermal spray techniques.....	22
2.2.1 Flame spray.....	23
2.2.2 HVOF (High-Velocity Oxy-Fuel spray).....	24
2.2.3 Detonation gun.....	25
2.2.4 Electric arc spray.....	26
2.2.5 Plasma spray.....	27
2.3 Plasma torch.....	31
2.4 Particles in flight.....	35
2.5 Splat formation.....	46
2.5.1 Particle impact velocity and temperature.....	48
2.5.2 Deformation, flattening degree, cooling rate.....	49
2.5.3 Heat transfer, thermal contact resistance.....	55
2.5.4 Substrate surface temperature.....	57
2.5.5 Splat solidification and microstructure.....	62
2.6 Coating build-up.....	66
2.7 Zirconia and alumina – materials in plasma spray.....	72
2.7.1 Zirconium dioxide – zirconia, ZrO_2	72
2.7.2 Aluminium oxide – alumina, Al_2O_3	79
2.7.3 Plasma spray applications of alumina and zirconia coatings.....	83

3.	MATERIALS AND EXPERIMENTAL SETUP.....	89
3.1	Yttria stabilized zirconia (YSZ) powder.....	89
3.2	Aluminium oxide (alumina) powder.....	91
3.3	Substrates – 316L stainless steel.....	93
3.4	Cross-section preparation and observation.....	94
3.5	Plasma spray system.....	95
3.6	SprayWatch monitor system.....	97
3.7	Laser flash method.....	102
3.8	Electrochemical impedance spectroscopy.....	105
4.	INFLUENCE OF SPRAY PARAMETERS ON PARTICLE VELOCITY AND TEMPERATURE.....	109
4.1	“Several parameters, one at a time” method.....	112
4.2	Taguchi design of experiment.....	124
5.	PLASMA SPRAYED SPLATS CHARACTERIZATION.....	135
5.1	YSZ splats, particle size (45 – 75) μm	136
5.2	YSZ splats, particle size (20 – 45) μm	139
5.3	Alumina splats, particle size (20 – 45) μm	141
5.4	YSZ and alumina powders plasma sprayed into water.....	149
5.4.1	SEM analysis of YSZ powders.....	150
5.4.2	SEM analysis of alumina powders.....	155
5.4.3	Raman spectroscopy.....	159
5.4.4	X-ray diffraction analysis.....	165
6.	PLASMA SPRAYED COATINGS CHARACTERIZATION.....	172
6.1	SEM observation of as-sprayed coatings.....	173
6.2	Porosity evaluation of YSZ and alumina coatings.....	179
6.3	Numerical model for the porosity assessment of the coatings.....	186
6.4	X-ray diffraction analysis of coatings.....	188
6.5	Thermal diffusivity measurements.....	192
6.6	Electrochemical impedance spectroscopy of the plasma sprayed coatings.....	196

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7. CONCLUSIONS.....207

REFERENCES.....211

APPENDIX 1: LIST OF PUBLICATIONS.....233

APPENDIX 2: LIST OF FIGURES.....234

APPENDIX 3: LIST OF TABLES.....239

ABSTRACT

The plasma spray technique is a highly sophisticated and effective surface treatment that has been successively used to produce protective coatings to improve component's resistance to corrosion, wear or heat in many industrial applications. Due to an increasing field of applications, along with more severe demands on coating properties, a remarkable change in the research concept of the plasma spray process has been noted. Previously, coatings of proper material properties were deposited and fulfillment of particular application requirements was examined. Recently, the individual stages of the plasma spray deposition process have been studied separately in order to establish the influence of main controlling parameters on the process; e.g., plasma formation, particle in-flight velocity and temperature, splat formation, coating properties, etc. Most of efforts were dedicated to study the electric arc fluctuations inside the plasma torch and their influence on formation of the plasma jet, the splat formation and change in the splat morphology. This led to the development of new plasma spray torches, diagnostic techniques and also advanced 3-D models.

In the present study, influence of different plasma spray deposition conditions due to the variation of several input parameters on the powder particle in-flight characteristics, splat formation and selected properties of $\text{ZrO}_2+8\text{wt.}\%\text{Y}_2\text{O}_3$ and Al_2O_3 plasma sprayed coatings were investigated. To monitor particle in-flight characteristics in the plasma spray process, an imaging diagnostic system equipped with a fast shutter CCD camera was used. Two statistical approaches were employed; i.e., (i) the “several

parameters, one at a time” method, and (ii) the Taguchi design of experiments method. It was found that the particle velocity and temperature could be changed significantly by selection of the input spray parameters. The particle velocity and temperature increased by 45 % and 14 %, respectively, during performed experiments. Net energy, spray distance and main gas flow rate were identified to be the most influential of the observed parameters. Influences of powder feed rate, auxiliary and carrier gas flow rates were not so prominent.

Three different sets of spray parameters were used for the deposition of YSZ and alumina splats and coatings onto the prepared 316 L stainless steel substrates at room temperature. Splats of different morphologies as well as un-melted or partially melted particles were found on the substrate surfaces. Increase in the particle velocity, usually enhanced by the higher particle temperature, resulted in more pronounced splashing and thinner splats. In case of the alumina particles, disk-shaped splats changed into splashed ones with an increase in the particle velocity. Degree of powder melting was assessed from powders plasma sprayed into water. It was found that the melt fraction of YSZ powder increased more than two times with the increase in net energy and decreased with the increasing particle size. Raman spectroscopy and X-ray diffraction confirmed higher content of the tetragonal zirconia and gamma alumina phases retained in powders that experienced melting in the plasma jet and subsequent rapid cooling in water. The amount of original zirconia and alumina phases dropped by 30 % after plasma spraying due to the formation of metastable phases.

Different splat morphologies caused by changes in the spray conditions were observed by SEM on the top surfaces of the YSZ and alumina thick coatings. Relative porosity of the coatings was estimated by a point count method from optical micrographs of the sectioned and polished coatings. With an increase in the particle velocity and degree of melting, the relative porosity of alumina coatings dropped from 23 % to 14 %. The relative porosities of YSZ coatings, due to the same change in the spray parameters, were reduced by a factor of two with the lowest porosity values above 20 %. XRD analysis showed drop of monoclinic zirconia phase by 30 % and residue of only 15 % of the original alpha alumina phase in coatings. Thermal diffusivity was measured by a laser flash method. Generally, the YSZ and alumina coating thermal diffusivities increased by 10 % and 28 %, respectively, with increase in the spray net energy. Results of the thermal diffusivity and porosity measurements were endorsed by electrochemical impedance spectroscopy measurements in terms of increasing electrical resistivity of the coatings and the pore resistance. Results were linked to the quality of interfaces inside the coatings, the decreasing porosity and the change in the pore size and shape.

1. INTRODUCTION

The most sensitive part of virtually any component from the point of view of failure is its surface. The surface, where the highest stress from the service loading is usually exerted, is furthermore directly exposed to an unfavourable action of environment. Different forms of surface degradation considerably restrict the usage of classical engineering materials for high-performance applications. One of the most prospective approaches to solve this problem is surface engineering that focuses on the development of specific surface modifications, which enable the suppression of these degradation processes. Forming a special layer or coating on the surface of the substrate, or changing the composition, microstructure or properties of the substrate surface layer by chemical, thermo-chemical, thermal or mechanical action, can lead to desirable properties of components' surface layers working in critical environments.

The thermal spray technology is one of the most pragmatic and highly cost-effective means of surface modifications. This technique is used to produce protective and functional coatings on a large variety of components mainly to increase the component resistance to corrosion, wear or heat. The coatings are prepared by using different spray processes such as plasma spray, high-velocity-oxy-fuel spray, cold spray, wire arc or flame spray process [1], [2], [3].

In the present work the plasma spray process has been used. In the plasma spray process the raw material, usually in the form of powder, is introduced into the plasma jet where it is melted and accelerated towards the substrate. Due to the high temperatures of

thermal plasmas any material can be melted and sprayed. Resulting droplets flatten, cool down rapidly and solidify upon impingement onto the substrate surface, forming so-called splats. Just as a wall is built brick-by-brick, the coating is built-up from individual splats giving the coating's structure a typical lamellar look.

The implementation of versatile and cost-effective plasma spray technique in manufacturing production, whether for its ability to provide superior functional properties or used to restore poor machined or worn surfaces back to specifications, can be traced back to 1960s. Plasma coatings were considered to be a repair or afterthought overlay to the component surface. Increasing demands on service of coated components under mechanical load in the severe environments has brought a need to tailor the coating properties according to particular application needs and in conformity with the component design. The effort to improve the plasma spray process was dedicated mainly to the development of new plasma torches, attempts in process diagnostics and optimalization and modelling of various phenomena involved in plasma spray process. At the beginning of the new century, most efforts are directed towards the development of closed-loop systems for an on-line control of the process (with the help of robust sensors having time resolution in the order of 100 μ s [6]) to improve coating reliability and reproducibility, as well as towards the implementation of new processes to achieve finely structured coatings, if not nano-structured ones [4].

1.1 Rationale

Plasma spray process can be divided into four sub-systems, each of them

comprising of large number of parameters and their interactions that determine the final coating microstructure and its properties [4]. The four sub-systems are:

- 1) plasma formation in a plasma spray torch,
- 2) injection of powder and its interaction with the plasma jet,
- 3) interaction of powder particle with the substrate surface and splat formation,
- 4) splat layering and coating build-up.

Plasma properties can be modified by the torch design (in particular the anode geometry and diameter of the anode nozzle) and by adjustment of parameters important for the plasma formation, such as types and flow rates of gases and net energy. Characteristics of powder injection (injector type, size and direction, powder feed rate, particle shape and size distribution, carrier gas flow rate) are important for interaction of powder with the plasma jet, affecting heat and momentum transfer from plasma jet towards the powder particles. Powder particle in-flight temperature (rather the molten state) and velocity, influenced by stand-off distance, powder and substrate material characteristics, substrate roughness, temperature and surface chemistry participate in the splat formation process. The coating formation and microstructure depend further on the relative velocity of torch and substrate, thickness of one pass and time delay between passes.

Coating properties depend totally on more than 50 spray parameters. Numerous studies described properties of many coatings according to their spray conditions, but attempts to link the particle parameters at impact, the formation of splats and coating and

the coating properties have emerged only a few years ago. As the database is very limited, it is still necessary to collect data on relative spray and in-flight parameters correlated to the coating service properties. This can be achieved, for example, by using factorial designs allowing to establish regression equations relating the coating properties to the particle parameters at impact and the coating formation temperature.

Fig. 1.1: Scheme of different stages in the plasma spray process.

Such a complete flow of understanding requires the necessity for the development of new plasma control and diagnostic methods and tools. The trend is now to create simplified on-line control systems, which work in harsh environments and allow

the follow-up of critical parameters such as particle temperatures, velocities and diameters upon impact in the spray process, in order to improve the process reliability and reproducibility. A real on-line control of the process requires establishing the corresponding data bank and expert systems. However, much is still to be done because, up to now, plasma processes have been studied almost independently of the product, which has been studied separately [4], [5], [6].

1.2 Objectives

Based on the above-mentioned rationale the aim of this study was defined as follows: attempt to find links and correlations between the major input plasma spray parameters and selected properties of zirconia and alumina plasma sprayed coatings through the investigations of different sub-systems of plasma spray process. The individual objectives can be summarized as below:

- Investigate influences of the fundamental plasma spray input parameters (namely net energy; main, auxiliary and carrier gas flow rates; powder feed rate and spray distance) on the powder particle in-flight characteristics
- Study the effect of different particle impact velocity and temperature on the splat morphology
- Characterize impact of the different plasma spray conditions on the porosity and thermal diffusivity of the coatings

1.3 Scope

Chapter 1 of this report provides reasons for necessity to study further the plasma spray technology. Short description of recent developments, pending problems and trends in research field of plasma spray are given. Complexity of plasma spray process, influenced by vast number of parameters, is indicated in rationale on which basis the objectives for the conducted experimental study were set.

Chapter 2 reviews fundamentals of thermal spray technology and basic spray techniques. Special attention is paid to plasma spray process and its sub-systems: plasma torch, particles in flight, splat formation and coating build-up. Review of material characteristics and plasma sprayed coating applications of alumina and zirconia is presented.

Chapter 3 describes materials, such as alumina, zirconia and 316L stainless steel, used in this experiment. Setup and description of used plasma spray system and particle in-flight monitor system together with description of some special experimental techniques (laser flash method, electrochemical impedance spectroscopy) are also provided. The flowchart of the experimental investigations as implemented in the present study can be found in Fig. 1.2.

Chapter 4 discusses the influence of fundamental plasma spray parameters on the powder particle in-flight velocity and temperature in the plasma spray process through the implementation of two different designs of experiment and proper statistical analysis: “Several parameters, one at a time” method and Taguchi design of experiments using the fractional factorial designs.

Fig. 1.2: Scheme flowchart of experimental investigations.

Chapter 5 is focused on SEM observations of alumina and YSZ plasma sprayed splats deposited on stainless steel substrates as well as on characterization and X-ray diffraction analysis of both powders plasma sprayed into water.

Chapter 6 characterizes alumina and YSZ plasma sprayed coatings through microstructure observations, measurements of coating porosity, XRD diffraction, thermal diffusivity and electrochemical impedance as related to the selection of input plasma spray parameters.

Chapter 7 summarizes results of all the observations and measurements into conclusions related to respective objectives that have been set at the beginning of the presented experimental study.

2. LITERATURE REVIEW

In this chapter, overall information about the thermal spray technology and different thermal spray techniques is given, followed by more detailed description of individual sub-systems of plasma spray process. Emphasis is placed on important process characteristics, material properties, their mutual correlations and effects on the plasma spray process. Review of material characteristics and plasma sprayed coating applications of alumina and zirconia is also presented.

2.1 Thermal spray technology

The thermal spray is a group of processes in which finely divided metallic or non-metallic materials are deposited in a molten or semi-molten state onto a prepared substrate to form a spray deposit [3].

In thermal spray processes, either chemical energy of gas combustion or electrical energy is used for melting of the sprayed material, which is fed axially or in a radial direction into the spray gun in the form of a rod, wire, powder or recently used liquid suspension. Melted material is then, by means of compressed gases, atomised to small particles (except for powders and suspensions). Air or controlled atmosphere surrounds the jet of molten or semi-molten particles propelled towards the substrate surface. Sometimes, spraying is conducted in a vacuum chamber to avoid the particle interaction with surrounding environment (esp. oxidation). Upon impinging the substrate surface, the melted particles flatten, spread and solidify rapidly, forming thin platelets. These

platelets, called splats, conform and adhere to irregularities of the prepared surface or to each other. Morphology of splats depends on the amount of thermal and kinetic energy of the impinging particle; kinetic energy is changed to heat and deformation energy. Generally, the size of splats ranges from few microns to over 100 microns in diameter and about $(1 - 20) \mu\text{m}$ in thickness. The thin splats undergo very high cooling rates, typically in excess of 10^6 K/s for metals. As the spraying gun is moved over the substrate surface, the coating is built up in particle-by-particle manner forming the characteristic lamellar structure of the plasma sprayed coatings. The coating is not homogeneous. Sprayed deposits usually contain some level of porosity (typically up to 10 %), lamellar voids, cracks and impurities (Fig. 2.1) [1], [3], [7].

Fig. 2.1: Typical coating cross section illustrating lamellar structure [3].

Surfaces to be thermally sprayed should be adequately prepared before spraying. Proper substrate preparation is the most critical step influencing the bond strength and the adhesion of the coating to the substrate. The following operations are the most important: cleaning, degreasing and roughening to provide irregularities and greater effective surface area.

The thermal spray technology is a pragmatic and cost-effective surface treatment of components in numerous branches of industry (e.g. chemical industry, power generation, aeroengine, automotive industry, steel manufacturing, glass industry, and many others; see Table 1). The protective and functional coatings of high performance materials are deposited on the component surfaces to provide the resistance against heat, wear, erosion and/or corrosion, as well as the unique sets of surface characteristics. As an example, thermal spray coating applications for aircraft turbine engine parts are shown in Fig. 2.2.

Fig. 2.2: Current and potential thermal spray coating applications for aircraft turbine engine parts [9].

A wide variety of materials can be used to produce coatings. In fact, any material that could melt can be used; i.e., the difference between its melting and decomposition or evaporation temperatures is preferably greater than 300 K (metallic as well as non-metallic, created by oxides, carbides, nitrides and other compounds, and also by combinations of various materials). The thermally sprayed coatings are also used to

restore worn and poorly machined parts to the original dimensions and specifications. A disadvantage, except for the size limitations, is the “line-of-sight” nature of these deposition processes. Only portions of component surfaces, that the gun “see”, can be coated [7], [8].

Table 1: Thermal spray coating properties of importance for various applications [8].

Industry sector	Wear						Thermal barrier	Corrosion/Oxidation
	Abrasive	Adhesive	Fretting	Erosion	Cavitation	Impact		
Aero gas turbines	X	X	X	X			X	X
Agriculture	X			X		X		
Architectural	X					X		
Automotive engines	X	X		X		X	X	X
Business equipment	X	X	X					
Cement and structural clays	X					X		X
Chemical processing	X			X				X
Copper and brass mills	X							X
Defence and aerospace	X	X	X	X	X	X	X	
Diesel engines	X	X		X		X	X	X
Electric utilities	X	X		X	X	X		X
Food processing	X							
Forging	X	X				X		X
Glass manufacture	X	X						X
Hydro-steam turbines	X	X	X	X	X			X
Iron and steel casting	X			X		X		X
Iron and steel manufacture	X			X		X		X
Medical	X		X					X
Mining and dredging	X			X	X	X		X
Nuclear								X
Oil and gas exploration	X	X		X		X		X
Printing equipment	X	X						
Pulp and paper	X				X	X		X
Railroad	X	X				X		X
Rock products	X					X		X
Rubber and plastics manufacture	X			X		X		X
Screening	X					X		X
Ship and boat manufacture/repair	X			X				X
Land-based gas turbines	X	X	X	X			X	X
Steel rolling mills	X	X						X
Textile	X							
Transportation	X	X					X	X

The current challenges in thermal spray technology, in particular the most used plasma spray technique, rest in the improvement of process reliability and reproducibility. In order to achieve this goal a lot of research is focused on behavior of the electric arc inside the plasma torch, development of new torches and powder feeding into the plasma jet followed by heat and momentum transfer towards the particles. Also modelling of particles in flight and upon impact onto the substrate has gained a lot of attention (3D models). Recently, new on-line monitoring systems of plasma spray process have been developed. However, to shift from monitoring to the close-loop control the sensors have to be connected to the spray torch control unit and relationships between coating properties and the particle parameters at impact with the coating temperature evolution have to be established [4], [5], [7], [9].

2.2 Thermal spray techniques

There are several variations of the thermal spray process, differing in the heat source, materials deposited and the final coating properties. A basic comparison of the typical characteristics of the various thermal spray techniques is shown in Table 2. The most important techniques are:

- Flame spray
- HVOF (High-Velocity-Oxy-Fuel) spray
- Detonation gun spray
- Electric arc spray

• Plasma spray

Table 2: Comparison of thermal spray processes [4], [10], [11].

Process	Gas flow m ³ /h	Flame or exit plasma temperature °C	Particle impact velocity m/s	Relative adhesive strength (*)	Cohesive strength	Oxide content %	Relative process cost(*)	Maximum spray rate kg/h
Flame powder	11	2200	30	3	Low	6	3	7
Flame wire	71	2800	180	4	Medium	4	3	9
HVOF	28-57	3100	610-1060	8	Very high	0.2	5	14
Detonation gun	11	3900	910	8	Very high	0.1	10	1
Wire arc	71	5500	240	6	High	0.5-3	1	16
DC plasma	4.2	5500	240	6	High	0.5-1	5	5
High-energy plasma	17-28	8300	240-1220	8	Very high	0.1	4	23
Vacuum plasma	8.4	8300	240-610	9	Very high	ppm	10	10
RF plasma	2-4	7500	60	-	-	-	-	6

*) 1 (low) to 10 (high)

2.2.1 Flame spray

The flame spray technique, sometimes called a combustion flame spray, uses the chemical energy of fuel gas (usually acetylene, hydrogen, propane or natural gas) and oxygen mixture combustion to melt the coating material. The feedstock material can be fed into the spray gun in the form of solid wire/rod, powder or, recently, liquid suspension. In torch in Fig. 2.3 the flame melts the end of a wire/rod, which is subsequently atomised by the compressed air to form droplets. These droplets form the stream and are successively propelled towards the substrate. The particle speed is relatively low (about 100 m/s), porosity can be high, and bond and cohesive strengths of the deposits are generally lower than those of the higher velocity thermal spray processes.

The ceramic rods, especially alumina and stabilized zirconia, were introduced in early 1950' when a demand arose for heat resistant refractory coatings. Resulting coatings were chemically inert, with lower porosity and harder than those prepared by flame powder spraying. The process is known as a Rokide, its name referring to the

ceramic rods labeling.

Fig. 2.3: Sketch of wires/rods flame spray technique [3].

2.2.2 HVOF (High-Velocity Oxy-Fuel spray)

In the HVOF process, the fuel is burnt with oxygen at a high chamber pressure, exiting through a small-diameter barrel to generate a supersonic exhaust gas jet. Fuel gases such as acetylene, kerosene, propane, propylene or hydrogen mixed with oxygen, are used as the working gas. The powder is injected laterally into the jet as a suspension in the carrier gas. The combustion chamber and nozzle are water-cooled.

Fig. 2.4: Sketch of high-velocity oxy-fuel spray torch [13].

Unlike in the flame spray technique, the combustion of gases is internal process,

and the gas flow rates and delivery pressures are much higher than those in the atmospheric flame spray processes. The combustion process minimizes thermal input and maximizes the particle kinetic energy to produce coatings that are very dense, with low porosity and high bond strength.

2.2.3 Detonation gun

The detonation gun differs from other combustion spray devices. It utilizes the energy of oxygen-fuel mixture explosions, rather than a steadily burning flame, to thrust powdered materials onto the surface of the substrate. The resulting deposits are extremely hard, dense, and tightly bonded.

Fig. 2.5: Detonation gun spray system [13].

The detonation gun, shown in Fig. 2.5, consists of a long water-cooled barrel into which a mixture of oxygen, fuel gas, and powdered coating material is introduced. When the gas mixture is ignited, a controlled detonation wave, or a flame front, accelerates and heats the powder particles as they propagate down the length of the barrel. After each injection of the powder has been discharged, a pulse of nitrogen gas purges the barrel and chamber. Multiple detonations (1 – 15) during each second build up the coating to

the desired thickness.

2.2.4 Electric arc spray

In the wire arc process, two consumable wire electrodes connected to a high-current DC power source, which are at first insulated from each other, automatically advance to meet at a point in an atomising gas stream. A potential difference applied across the wires initiates an arc that melts the tips of the wire electrodes. An atomising gas, usually compressed air, is directed across the arc zone, shearing off the molten droplets that form the atomised spray and propelling them towards the substrate. If the wires are of different materials, pseudo-alloy coatings can be produced. The process is energy efficient because all of the input energy is used to melt the metal. The limitation of the process is electric conductivity of the coating material. The spray gun is illustrated in Fig. 2.6. The wire electrodes are fed through the wire guides and into the contact tips. The atomising nozzle conducts the compressed air and directs it across the arc zone.

Fig. 2.6: Sketch of an arc spray gun [3].

The arc temperatures considerably exceed the melting point of the spray material. During the melting cycle, the spray metal is super heated to the point where some volatilisation may occur. The high particle temperatures produce metallurgical

interactions or diffusion zones, or both, with the substrate after impact. These localized reactions form minute weld spots with good cohesive and adhesive strengths. Thus, the coatings develop excellent strengths.

2.2.5 Plasma spray

Thermal plasmas are commonly generated in inductively coupled discharges (inductively coupled plasma – ICP, radio frequency plasma - RF) or in direct electric arcs (direct current - DC) that are stabilized by flowing gas or water vortex. Physical processes that determine properties of differently generated plasmas and basic torch characteristics are described below.

2.2.5.1 DC plasma torch with gas stabilized arc

In the DC plasma spray torch, using the arc gas stabilization, gas or a gas mixture is passed through an electric arc between a coaxially aligned tungsten cathode and an orifice in a copper anode (Fig. 2.7). The gas is superheated by DC arc and partially ionised, producing plasma. As the plasma exits the gun, the ions recombine with electrons and liberate energy for heating of the spray material. Average plasma temperatures in torches with gas arc stabilization are usually in the range from 8 000 K to 14 000 K. Average plasma enthalpies, determined as ratio of the useful power of the plasma generator to the flow rate of the plasma forming gas, vary from 1 to 30 MJ/kg [11], [12]. The powder is introduced into the plasma, melted, and propelled onto the workpiece by a high velocity stream. The heat content, temperature, and the velocity of the plasma jet are controlled by the torch geometry, the arc current, the mixture ratio

of gases, and the gas flow rates.

Fig. 2.7: Sectional view of a plasma torch with gas-stabilized arc [3].

2.2.5.2 DC torch with water stabilized arc

In plasmas with gas stabilization the further increase of plasma temperatures and enthalpies is limited by the fact that flowing gas protects the arc chamber walls from thermal overloading and thus a minimum possible gas flow rate exists for given arc power. Higher thermal loading is possible if the walls are created by liquid and an arc is stabilized by wall evaporation. Thus, water-stabilized arcs can be utilized as sources of thermal plasmas with higher temperatures up to 50 000 K and enthalpies of about 300 MJ/kg [11], [12]. High flow velocity (about 8 km/s) combined with very low ratio of plasma density to the density of ambient air leads to intensive turbulent mixing of flowing plasma with ambient gas and thus to rapid decrease of temperature and velocity along the jet.

The schematic picture of plasma gun with water-stabilized arc is shown in Fig. 2.8. Water is fed tangentially into an especially shaped chamber where it creates a swirl. Water flows over the segment which determines inner diameter of the vortex into the exhaust slot. An arc is ignited in the center of water vortex between the graphite cathode within the chamber and the rotating anode outside the chamber. Evaporation of water together with heating and ionization of vapour are principal mechanisms that produce plasma jet. Feedstock material is introduced into the jet outside the torch.

Fig. 2.8: Schematic of plasma gun with water-stabilized arc [12].

2.2.5.3 Inductively coupled plasma torch

In inductively coupled plasma torch, a water cooled helix of several turns, usually three or four, is wrapped around a quartz tube that is closed at its top end and fitted with two inlet ports to feed a spray material and a plasma forming gas (Fig. 2.9). The plasma gas is introduced inside the intermediate tube that gives a flow pattern to a high velocity sheath gas flowing close to the inside wall of the quartz tube in order to reduce heat losses and to protect it from overheating. When the plasma gas is released into the tube, copper helix is energized by a high frequency current resulting in an intense magnetic

field inside the tube that causes ionization of the gas. Continuous feeding of the gas causes it to escape through the open bottom of the tube. Powder fed into the plasma filled tube is melted and relying on either gravity or the plasma flow is conveyed to the work surface [14], [15].

Fig. 2.9: Schematic of inductively coupled plasma torch.

Coatings produced by RF plasma technique have shown to be generally homogeneous and not porous. Among important advantages of this technique are ease of powder injection, longer residence time in the plasma and better melting of the powder particles. On the other side is the difficulty of manipulation to spray a component of complicated configuration.

Currently several new spray processes are also used [7], [10]: underwater plasma spray, high or low pressure plasma spray, high-velocity air-fuel spray, solution precursor

plasma spray (SPPS) and others. Also cold spray technique has its origin in thermal spray processes. It is based on the acceleration of powder particles to supersonic velocities (300-1 200 m/s), and hence high kinetic energies, using the convergent-divergent, de Laval nozzle, high pressure and flow rates of gases. The solid-state plastic deformation and fusion occur on impact to produce dense coatings without the feedstock material being significantly heated.

From all of the thermal spray techniques, the atmospheric DC plasma spray seems to be the most employed and studied. DC plasma spray technique with gas stabilized arc was also employed in the presented study; therefore, the following discussion will pertain to this spray technique.

2.3 Plasma torch

In the plasma spray torch, DC arc is struck between the tip region of the cathode and the internal surfaces of the water-cooled anode. Fig. 2.10 shows the principle of the plasma jet generation. Electrons, emitted from the cathode tip, are accelerated by the electric field and form the plasma column that expands through the nozzle and is stabilized by the plasma-forming gas flow. Due to the fast expansion of plasma column, surrounding air is pumped into the plasma column. In case that the boundary layer close to the wall is hot enough, small arc columns hit the anode, striking from the main plasma column which develops more or less parallel to the nozzle wall. Because of magnetic and drag forces, these arcs are traveling along the nozzle wall. The arc root speeds fall in the range of (50 – 100) m/s. The range of the arc root motion as well as the arc root speed

in eroded anode drops to less than one half of those for a new anode. This observation can be explained by a tendency of the arc root to stay at certain preferred spots on an uneven surface of the anode. In order to avoid damage at the anode due to the local high temperatures and erosion effects and in order to stabilize the arc, the axially introduced plasma gas is given a tangential spin by a gas distribution ring at the burner inlet. Parameters controlling the plasma column expansion are the injected plasma gas composition, the mode of injection (vortex or parallel to the cathode), gas flow rate; the shape of cathode tip and surrounding nozzle [16], [37].

Fig. 2.10: Plasma jet generation [16].

Arc instabilities in the plasma spray torches can significantly affect the quality of plasma sprayed coatings. Instabilities in the arc are best reflected by voltage fluctuations. A direct effect of the arc voltage fluctuations on the particle in-flight characteristics was studied in [38]. Using SG-100 spray gun, it was found that with the increasing current and secondary gas flow rate, the coating qualities can be improved due to a longer plasma jet and better heating of sprayed particles. A strongly eroded anode significantly reduced

the jet length, resulting in poor particle heating and coating porosity increase. Accordingly, different anode conditions require a different set of values for the operating parameters for optimal torch operation.

Depending on the material to be sprayed and the plasma gun used, the plasma-forming gas is pure Ar, Ar-He, Ar-H₂, N₂-H₂ or Ar-He-H₂ mixture. The various spray gases contain always heavy gas such as argon or nitrogen to achieve the high gas momentum. Argon, the inert gas, is recommended as the primary gas because it will not react with the powder or substrate during plasma spraying. Argon is less aggressive towards cathode and anode and has a low ionization potential allowing for an easy arc ignition. A disadvantage of using argon is that the heat content of an argon plasma stream is lower as compared to a nitrogen plasma stream. Therefore, a small percentage of nitrogen is added to the primary gas (argon) to increase the heat of the plasma to melt the powders completely. Nitrogen also helps to push and stabilize the arc root downstream in the anode nozzle, and accelerates the particles without using a too high gas flow rate. However, during plasma forming with nitrogen, nitrous gases will be generated (nitrogen oxide) which can be hazardous to personnel. When dissociation (between 3 000 and 5 000 K for H₂ and O₂, 6 000 and 8 000 K for N₂) or ionization (between 8 000 and 16 000 K for Ar, N₂, O₂, H₂ and 12 000 and 26 000 K for He) occur, the enthalpy and sound velocity exhibit strong variations and plasma specific heat and thermal conductivity exhibit peaks. The highest values of thermal conductivity are obtained over 3 000 K for H₂ and 12 000 K for He. Thus, plasma gas mixtures contain very often one of these two gases to enhance the heat transfer to the particles [18].

DC plasma jets are characterized by high temperatures (up to 14 000 K), velocities (up to 2 200 m/s), high heat fluxes (up to 10^{10} W/m² in the plasma core), reduced dimensions (<10 mm), steep temperature gradients (up to 10^7 K/m) as well as velocity gradients (up to $5 \cdot 10^5$ m/s) and the important fluctuations in the 0.1 ms range. Plasma temperature and velocity depends strongly on arc current used.

Fig. 2.11: Main regions of a transient plasma jet [18].

As it can be seen in Fig. 2.11 the flow is highly turbulent, which can be explained by the large density differences between the plasma gas and the surrounding air. These density gradients are causing a long core region and a delayed mixing of the plasma gas with the surrounding air. Behind the nozzle exit, swirls are developed along the jet fringes and eddies of cold air are entrained into the plasma gas. Further downstream in the plasma jet, these eddies break down, being dragged towards the jet centerline

resulting in a fully turbulent flow. The powder particles are injected into the plasma flow and exposed to large temperature and velocity fluctuations during their flight where they receive heat and momentum transfer from the turbulent flow consisting of the hot plasma gas and entrained air. With typical arc root fluctuations of 5 000 Hz and particle residence time of 1 ms (given by plasma jet length and particle velocity) powder particles will experience up to five hot plasma “puffs” [4], [6], [18].

Influences of various modifications of the plasma spray torch assembly on plasma spray process have been investigated. Difference in the microstructure of YSZ coatings related to the anode exit shape of used plasma torch (Laval-like contour and cylinder) was investigated in [19]. Influence of carrier gas axial feeding on the plasma axial and radial temperature distributions was observed in [17].

2.4 Particles in flight

Size, shape and density of powder particles are important, and correlated, characteristics determining powder performance in the carrier gas flow and plasma jet [20]. The *shape* of powder particles controls powder flowability and sprayability, and thus, unmelted particles in the coating, porosity, vaporization, and so forth. The particle shapes can vary greatly, from spherical shapes to irregular or acicular shapes. Irregularly shaped particles do not feed as easily as spherical powders. They can pack together and, especially at lower carrier gas flow rates, result in choking of the feeding hose or in accumulation of packed molten material at the injector nozzle exit blocking so the passage of the plasma jet [22], [23], [24], [30].

The powder particle *density* is a rather loosely used term in the plasma spray variously used to define the absence of porosity, the specific gravity of a material, and the apparent density of powder. Apparent density includes all the spaces between particles and pores within the powder particles themselves. The apparent density affects powder feed rate, trajectory, acceleration and heating in the plasma jet. Denser particles are more resistant to the horizontal drag force; they spend more time in the plasma jet, which is favourable for the plasma spray process. Particles of low density material require a high carrier gas flow rate for their transport into the plasma jet, which may affect the plasma jet. This depends on the relative momentum of the gas flows and the location of the injector [21], [22], [29].

The particle *size* can influence the depth of particle penetration into the plasma jet, resistance to drag force, degree of particle melting etc. The smaller particles may not enter the plasma jet, due to the insufficient momentum. Instead, these smaller particles will bounce off the plasma jet and be lost as waste particles or may become embedded in the coating as the unmelted particles. If the carrier gas flow rate is increased to compensate for the low weight of the small particles, the increased velocity, at which the particles enter the plasma, may cause the larger particles to be propelled through the plasma, due to an increase in their momentum. Therefore, powders of narrow particle size ranges are preferred to ensure more uniform particle velocity and temperature distributions [18], [21], [31].

The powder is injected locally in the plasma jet through one or two injectors by means of a carrier gas. The *injection* geometry (injector design, position and angle with

the torch centreline) and interaction of the particles flow in carrier gas with the plasma jet control, to a large extent, the distribution of particle trajectory in the plasma jet, and therefore, their acceleration and heating. In most cases, the injector is orthogonal to the jet axis either inside the anode-nozzle (downstream of the arc root) or outside it. The typical injector internal diameters range between 1.5 and 2 mm. The smaller injector diameter results in a higher particle injection velocity, and thus, a deeper penetration of the particles in the plasma flow. During the pneumatic transport of the powder particles through the injector, they collide among themselves and the injector walls. Therefore, they cannot attain full velocity of the carrier gas. These collisions are also responsible for the particle jet divergence at the injector exit, especially for particles with the diameters below 20 μm [18], [21].

The *carrier gas flow rate* determines the rate at which the particles are injected into the plasma for melting. The flow rate must be sufficient to propel the particles from the hopper to the plasma. If the carrier gas flow rate is too low, the gas will simply pass over the powder in the feed tube, delivering little or no powder with poor inertial penetration in the plasma jet. The deflection of the plasma jet can occur as soon as the carrier gas mass flow rate, for internal injection, corresponds to 10% of the plasma gas flow rate. Thus the carrier gas flow rate must be optimized so as to correctly inject the powder into the plasma jet. Due to the radial injection of powder some of the particles might be transported on the periphery of the plasma stream and do not melt sufficiently prior to impact. Generally three cases, as shown in Fig. 2.12, with different flow rates of carrier gas can be observed. When the flow rate is too high, the powder particles will be

propelled through the plasma stream and carried on its periphery. If the flow rate is too low, the particles will bounce off the plasma stream, not having enough momentum to penetrate it. Optimally, the particles should be injected into the plasma jet so that they can be carried along its center to the desired substrate area. The dependence of particle trajectories on injection conditions is more marked for fine particles and/or low density materials [3], [18], [21], [22], [42].

Fig. 2.12: Effect of a carrier gas flow rate on particle penetration into the plasma jet.

Loading of powders into the plasma jet will affect the flow's axial velocity and temperature fields. For high powder injection rates, the presence of the powder will have two effects. First, the heat extracted by the powder from the plasma could cause substantial local cooling of the gas. Secondly, depending on the type of powder, the evaporated fraction of the particles diffuses in the plasma gas, and can drastically change its thermodynamics and transport properties. It has been shown that plasma temperature and velocity may drop significantly already for powder mass flow rates in the order of one third of the plasma gas mass flow [27], [28], [33], [34], [35], [36], [39].

Other factors that affect the in-flight characteristics of powder particles are the *dwelt time* and the distance which the particle penetrates within the plasma jet. The plasma jet with particles has a conical shape. The real plasma jet temperature and velocity change in the axial and radial directions. The jet is usually divided into two

zones: a core zone (with high temperature and high velocity, where the ambient gas has not penetrated into the plasma yet) and a developed zone (region of decaying temperature and velocity, where the ambient gas mixes with the plasma gas). When the particles penetrate the plasma jet core, they are first heated and accelerated. Then, in the plasma plume, they decelerate and slowly cool down. Particles have a residence time in the millisecond range and receive a heat flux as high as 10^8 W/m^2 . As a result of the high gradients in the plasma jet, particles, which follow different trajectories, will have different acceleration and heating. Also, for large particles of low density and low conductivity materials, the rate of heat conduction in the particles may be too slow to ensure a homogeneous heating and melting during residence time of the particles in the plasma jet [3], [18], [39].

Particles can react in flight with the plasma gases or surrounding gas, which mixes with the plasma jet, and undergo chemical reactions, decomposition and evaporation. In addition, the large difference between particle and flow velocity may induce convective movements within the molten droplets, at least for materials with melting temperature below 2 300 K. This results in a continuous renewing of the liquid material at the particle surface. For metal or alloy particles sprayed in the air this liquid movement brings about a high oxidation rate enhanced by the presence of atomic oxygen in the plasma flow [40].

The goal pursued while optimising the process parameters of spraying is to ensure that all particles impacting the substrate are molten and have maximum possible velocity [1]. As a result, the smaller particles will tend to develop a larger degree of superheat, becoming subject to *vaporization*. Moreover, to melt large particles and/or poorly heat

conducting particles it might be necessary to choose process conditions that lead to an intensive evaporation from the particles surface. This is a result of the temperature gradients inside the particles. It was also suggested that the particle temperature could be affected by a huge latent heat of evaporation [39]. However, the effect of evaporation is not desirable for the following reasons [1]:

- Evaporation reduces a productivity of the process (defined as the ratio of the mass of material deposited to the mass of material sprayed).
- Vapour cools down the plasma jet around the particles reducing the heat transferred to them.
- Condensation of the vapour on the coatings just deposited may reduce its cohesion and toughness.
- Vapour of some materials (e.g. Cr_2O_3) is dangerous to health.

The most important particle parameters influencing the splat formation in the plasma spray process are *velocity* and *temperature* of the impacting particles. The ability to measure these parameters during the particle flight in a plasma stream could allow prediction of the produced coating characteristics. It is very difficult to define corresponding relationships between the splat morphology and the particle in-flight velocity and temperature because they are complex functions of particle trajectory in the plasma jet and plasma operating conditions [48]. In the following paragraphs, influence of some plasma spray parameters on the particle velocity and temperature will be addressed.

A significant factor concerning the raw powder material entering the plasma spray process is the powder *particle diameter*. Generally, small powder can be easily melted and accelerated to high velocity [77]. As it was shown in [78] the smaller/lighter particles achieved higher average particle velocity than the larger/heavier particles. The temperature decreased slightly when the particle diameter increased. Different velocities of the molten powder particles during their flight may result in their frequent collisions and agglomeration. The agglomeration results in an increase of the particle diameter [1]. Interesting results were obtained in [52], where particle position in the plasma jet was considered. It was much easier to heat the small particles, in the colder zones of the plasma jet, while the big particles travelling over the optimum trajectory were more difficult to heat in spite of a slightly longer residence time. Influence of particle diameter on in-flight velocity and temperature can be observed in Fig. 2.14 and Fig. 2.15.

The *powder feed rate*, partially discussed above, is another parameter affecting the particle in-flight characteristics. The decrease in velocity and temperature with increasing powder feed rate is clearly understood from the fact that the same total enthalpy of thermal plasma has to be distributed among a higher spray particle density which decreases the effective heat and momentum transfer to each particle. In addition, the particle velocities at the injector exit are weaker. Therefore, the penetration of particles into the plasma jet is more difficult and they are shifted away from the optimum mean trajectory. Increasing the particle velocity by reduced feed rate will cause improved coating performance on one side (low porosity, high hardness). In opposite, lower feed

rate will reduce also the economy of the process by reduced deposition efficiency. A compromise between both, that can be defined by a certain operation window in the particle velocity, has to be found [52], [79].

Raising up the *power* or *arc current* delivered to the torch results in increase of the particle temperature and velocity [52], [78], [80], [82], [83]. High torch input power is apt to heat the particles better but at the same time it also accelerates them faster. As the result, the increase in torch power cannot elevate the particle temperature too much because of the shortened particle dwelling time in the plasma jet.

Fig. 2.13: Velocity distributions of sprayed particles as a function of ambient pressure at different spray distances. The particle velocities increase as the pressure drops and the rapid increase of particle velocity is observed at below 150 torr (modified from [83]).

The same problem with the shortened dwelling time and the insufficient melting of the powder particles was observed in [80] and [83], where the particle velocity and temperature were controlled by changing *chamber pressure* (Fig. 2.13). As the chamber

pressure increased, the plasma flame shortened. The particles slowed down and at the same time the particle temperature increased. In [80], increase of the particle temperature improved the deposition efficiency, the density and the hardness of the zirconia coatings. On the other hand, excessive increase of the particle velocity above a certain value resulted in decrease of observed coating properties. The shortened dwelling time of the particles in the plasma jet prevented the powder core from melting, even if the surface was sufficiently heated.

One of the strongest factors influencing the particle velocity and temperature is the *spray distance* (stand-off distance). The average stand-off distance is about 120 mm. In spite of the fact that cold particles are rapidly accelerated and heated in the early stage of the plasma spray, later both effects decrease with increasing spray distance. The steep increase of the particle velocity in the region of short spray distances, where the sprayed particles are accelerated by the momentum exchange with the plasma particles, comes from the fact that the plasma jet is very fast here. Beyond this region, where the plasma jet velocity is considerably reduced, the accelerated particle velocity decreases slowly due to the higher momentum of the sprayed particles as compared to the particles of the plasma gas and due to air resistance (Fig. 2.14) [48], [78], [83], [84]. The effect of the stand-off distance on the splat morphology was taken into account in the study with partially stabilized zirconia [69]. On average, the longer the stand-off distance, the fewer smooth circular splats were observed. At short stand-off distances, there were a significant number of circular splats, all having a fine crack structure. The percent of circular splats decreased as the stand-off distance increased, as an evidence of partially

molten particles became dominant in a particle stream.

Fig. 2.14: In-flight velocity and temperature of nickel particles measured at various spray distances (modified from [50]).

The effects of the hydrogen, total gas and carrier *gas flow rates* on particle velocity and temperature were studied in [78] (Fig. 2.15). Hydrogen flow had significant influence on the average particle in-flight characteristics. The average particle temperatures and velocities were observed to increase rapidly with increasing hydrogen flow rate, following the same trend. The increase in the total plasma gas flow produced a decrease in the average particle temperature. However, by increasing the gas flow, the velocity of the gas exiting the plasma torch increased. The increase in gas velocity is then transferred, to the injected powder particles, increasing their average velocities. The carrier gas had an almost imperceptible effect on the average particle temperature and only a small effect on the average particle velocity. Once the carrier gas flow rate had

reached the level necessary for powder to penetrate into the plasma, no significant increases were observed.

Fig. 2.15: Plots illustrating effects of gun current, H₂, total gas and carrier gas flow rates and axial spray distance on the average temperature and velocity of partially stabilized zirconia particles; values are normalized in respect to highest value measured (modified from [78]).

In the plasma spray process, propelled powder particles are in principle deposited in a layer-by-layer manner onto the prepared component surface. Therefore, the deposition process consists of two stages [41]:

- Formation of a single splat
- Building-up of a coating (usually using few passes of spray gun) by depositing splats on the substrate or previously deposited droplets.

2.5 Splat formation

Upon impacting the substrate, the high momentum molten particles deform and solidify rapidly forming lamella called splat. The splat formation process is affected by many parameters [41], [44], [45], [46], [47]:

- Particle parameters at impact: position/trajectory in the plasma jet, size, temperature (molten state), velocity, impact angle, surface chemistry, material.
- Substrate (or previously deposited layer) surface parameters: contamination by condensates and absorbates, oxidation state, topography, temperature, thermal properties.

These all are important variables that affect the morphology and microstructural characteristics of single splats. The formation of splats of different shape, thickness and quality of contact with the substrate or the previously deposited layers will control the nucleation phenomenon, and thus, the coating crystalline structure, the quenching

stress and the coating adhesion-cohesion as well as the thermo-mechanical properties.

Assume a droplet impacting onto a flat, dry, and relatively smooth surface. On impact, due to the stored kinetic energy, pressure in the particle increases, and thus, a thin symmetric sheet of fluid begins to jet radially outward over the solid surface. Depending on a number of factors, the leading edge of this sheet may become unstable soon after the impact, resulting in the emergence of very regular undulations. Such undulations were found in photographs taken from beneath a transparent surface [46]. Where the undulations continue to grow they may begin to resemble fingers. The flattening splashing results in extensively fingered splats; the fingers have a poor adhesion with the substrate or the previously deposited layers. It was suggested that except the flattening splashing, the impact splashing is another kind of splashing in a plasma sprayed splat formation process [67]. Impact splashing results in the ejection of tiny droplets ($1\text{ }\mu\text{m}$) in the impact direction and seems to occur immediately after the particle collision with the substrate. The splashing phenomena play an important role concerning the contact quality between splats and underlying surface; i.e., the coating adhesion/cohesion.

It is commonly believed that the splat fragmentation is detrimental to the coating quality, affecting not only the splat solidification rate but also the phase selection, deposit microstructure development and deposition efficiency [68]. The impact of a single droplet in the plasma spray is a non-reproducible event, thus splat formation and splashing require more attention in order to refine known general tendencies through experiments and modeling. In the following paragraphs description of the basic

influential parameters and their correlation with the splat formation process together with some possible hypothesis for the formation of either splashed or disk-shaped splats will be given.

2.5.1 Particle impact velocity and temperature

It is obvious that the particle velocity has a significant impact on the splat morphology. Particle kinetic energy is transformed into deformation energy and heat. Molten particle with the right amount of kinetic energy will form a regular disk-shaped splat and anchor onto the surface upon striking the substrate. The excessive particle velocity produces splats with distinctively raised rims or even broken edges surrounded by small droplets. Broken edges and raised rims are usually considered to be detrimental to the coating quality forming asperities for consequently deposited particles influencing thus flattening, splashing, interface contact, cooling rate, coating porosity etc. On the other hand, certain amount of features leading to higher coating porosity can be desirable in applications such as TBCs or to improve thermal shock resistance [3]. Both possible splat morphologies, disk-shaped and splashed splat, for alumina are shown in Fig. 2.16.

It is notable that a few small disk-shaped splats can be formed even though the majority of the splats are fragmented, indicating the dependence of the splat morphology on the droplet size [47]. Generally, at a low velocity, disk-shaped splats are obtained. With increasing particle velocity, the impacting droplets flatten and spread more, producing thinner and bigger splats, providing larger contact area with the substrate and resulting in higher cooling rate. Higher flattening degree of the molten

particle is also subjected to the particle temperature. With increasing particle temperature, material viscosity decreases which enables better spreading resulting in better splat - substrate contact, and thus, higher particle cooling rate, adhesion/cohesion and residual stresses.

Fig. 2.16: Two different alumina splat morphologies: disk-shaped and splashed splat (diameter of about 50 μm).

2.5.2 Deformation, flattening degree, cooling rate

The flattening behavior of the plasma sprayed particles has been investigated extensively by theoretical, analytical and experimental approaches [45], [49], [50], [51], [52], [53], [54], [55], [56], [57], [58], [59]. Basic factors used for evaluation of the splat flattening and formation processes are summarized below (Fig. 2.17).

- Equivalent diameter ED ; represents the diameter of a circle having the same area as the selected feature

$$ED = \sqrt{\frac{4A}{\pi}} \quad (1)$$

- Elongation factor EF ; characterizes the non-circular nature of a feature, unity being a perfect circle

$$EF = \frac{\pi L^2}{4A} \quad (2)$$

- Degree of splashing DS ; estimates peripheral projection of material, unity resulting from the absence of such projections

$$DS = \frac{P^2}{4\pi A} \quad (3)$$

- Degree of flattening DF ; an evaluation factor that represents the flattening behaviour of the sprayed particle

$$DF = \frac{D}{D_0} \quad (4)$$

- Reynolds number R_e ; a measure of the droplet inertia to viscous force

$$R_e = \frac{\rho V_0 D_0}{\mu} \quad (5)$$

- Weber number W_e ; a measure of inertia to the surface tension force

$$W_e = \frac{\rho V_0^2 D_0}{\gamma} \quad (6)$$

- Ohnesorge number O_h ; a measure of surface tension forces

$$O_h = \frac{\sqrt{W_e}}{R_e} = \frac{\mu}{\sqrt{D_0 \gamma \rho}} \quad (7)$$

The effect of solidification is to reduce the degree of maximum spread. The degree of reduction is dependent upon the ratio of Stefan and Prandtl numbers [45].

- Stefan number S_{te}

$$S_{te} = \frac{C(T_m - T_s)}{H_f} \quad (8)$$

- Prandtl number P_r

$$P_r = \frac{\nu}{\alpha} \quad (9)$$

In the equations above A is the area, L is the longest dimension and P is the perimeter of the selected feature, D_0 is the initial droplet diameter, D is the splat diameter, V_0 is the impact velocity, ρ is the liquid density, μ is the liquid viscosity, γ is the liquid-gas surface tension, C is the droplet heat capacity, T_m is the droplet melting temperature, T_s is the initial substrate temperature, H_f is the latent heat of fusion, ν is the droplet kinematic viscosity, and finally, α is the droplet thermal diffusivity.

Fig. 2.17: Illustrations of selected splat characteristics [54].

The equivalent diameter is an absolute number whereas the elongation factor, the degree of splashing and the degree of flattening are ratios where a number greater than unity represents an increase in the tendency to elongate, splash or flatten, respectively. There have been several successful attempts to derive analytical expressions of flattening degree represented as a function of Reynolds and Weber numbers [45], [54]. Since these two numbers are functions of particle velocity and temperature, the diagnostics of in-flight characteristics of the particle stream is important for prediction of the particle flattening behavior.

In [52], the decrease of flattening degree of larger particles, as compared to smaller ones, is explained by lower temperature of the larger particles impinging the substrate. Spreading of the molten material is then limited because of the higher viscosity. However, the decrease in flattening degree can be compensated by increasing particle splashing on substrates kept below so called transition temperature. On both, the high and the low temperature substrates, the flattening degree increases steadily with the particle temperature as the viscosity diminishes. It was found that the final flattening degree, the flattening velocity and the flattening acceleration of the splashed splat were higher than those of the disk shaped splat [59]. Actual values of the particle flattening degree, after spraying at substrate temperatures of 100 and 400 °C, for alumina and YSZ were determined in [51] to be (1.5 to 2.6) and (1.2 to 2.3), respectively. Lower values in case of YSZ are caused by its lower thermal conductivity. Flattening degree above 3 was measured for YSZ splats sprayed on glass at 600 °C, at which substrate temperature most of the splats were disk-shaped [55]. The flattening degree increased with the increase in

velocity and slightly increased with the increase in temperature, especially below the melting temperature of zirconia, which might be due to the super-cooling effect. The measured deformation time (3.3 – 5.6) μs decreased with the increase in velocity and temperature, and increased with the increase in droplet diameter. The cooling rate was in the order of $10^6 - 10^8$ K/s. There was no obvious relation of the cooling rate with the impact velocity and temperature of the particle but clear relation with the droplet diameter. Different values of the cooling rate for the splats sprayed at different substrate temperatures were reported in [57]. The overall splat cooling rate is significantly higher for the hot substrate system as compared to the cold substrate sample. The average cooling rate of the partially stabilized zirconia splat was about 600 and 150 K/ μs on stainless steel substrates kept at 573 and 373 K, respectively. This can be attributed to a change in the wettability of the flowing material or substrate surface chemistry when the substrate is preheated to elevated temperature. This change favours a more intimate contact between the splat and the underlying surface, as confirmed by the change in splat morphology. When the steel substrate temperature is low or its surface too oxidized, the physical contact between the splat and the surface is limited [65].

The cooling rate, linked to the quality of the contact between the splat and the substrate (or underlying layer) and the splat thickness, controls nucleation and thus crystalline structure [41]. The splat thickness is, in fact, involved in the definition of the flattening degree: for a particle of a specified mass, an increase in this degree will result in a diminution in splat thickness resulting in a faster cooling. Therefore, the evolutions of the cooling rate and flattening degree must roughly follow the same

Fig. 2.18: Pictures representing evolution of the cooling rate and flattening degree with the particle velocity, size and temperature, respectively, for zirconia particles sprayed onto 304L stainless steel mirror-polished ($R_a < 0.1\mu\text{m}$) substrates at 75 and 300°C (below and above the transition temperature) [52].

trends; see Fig. 2.18 [52].

Diagrams in Fig. 2.18 show the evolution of the cooling rate with the particle velocity, size and temperature for two substrate temperatures. When the substrate is kept at 75 °C, the cooling rate is almost constant while it increases regularly when the substrate temperature is 300 °C. In the former case, the heat transfer to the substrate is dominated by the poor interfacial thermal contact while in the latter case, the thickness of the splat will mainly control the cooling process as the good interface contact is not a barrier to heat transfer. An increase in the particle temperature comes along with a decrease in material viscosity and, therefore, in the splat thickness (in both cases the cooling rate increased with the particle temperature).

Deformation and solidification of the super-cooled particles under plasma spray conditions were investigated in [56]. It was found that super-cooled droplet finishes flattening much earlier due to the higher viscosity and is completely solidified at around half time of the super-heated one. The difference in deformation degrees will substantially alter the final splat thickness. Therefore, the structure of the coating will be greatly affected by a small difference in the deformation degree. The deformation degree of super-cooled droplets increases also with the higher initial droplet temperature and the impact velocity. The deformation time does not depend upon the substrate temperature but the solidification time is greatly affected by the temperature.

2.5.3 Heat transfer, thermal contact resistance

The solidification of the molten particle is due to the rapid energy transport from

spreading particle towards the substrate. In the most typical conditions, the solidification process starts at the interface between the particle and the substrate (or previously deposited coating). The substrate plays the role of a heat sink from the splat at high temperature. There are both phases of liquid and solid inside the splat during flattening [53]. The solidified part of the splat becomes thermal conduction medium from the molten phase to the substrate. The temperature of the residual liquid increases due to the liberation of latent heat of fusion. In the liquid part of the splat convective heat transport is dominant because of high velocities of fluid flow. Estimates of the heat loss by convection from droplet surface to the surrounding gas showed them to be three orders of magnitude lower than that to the substrate [64].

The heat transfer coefficient can be calculated using the following formula [55]:

$$h = \frac{C_p \rho t}{C_R (T_p - T_s)} \quad (10)$$

where C_R is the cooling rate, C_p is the specific heat of an particle, ρ is the particle material density, t is the splat thickness, T_p is the particle impact temperature, and T_s is the substrate temperature. The estimated value for zirconia at 600 °C glass substrate was in the order of $3.10^4 - 3.10^5$ W/m²K (C_p used was 87.864 J/molK) [55]. The thermal contact resistance is an inverse number of the heat transfer coefficient. The splat flattening degree decreases as the solidification rate increases. Maximum particle spread is sensitive to the magnitude of thermal contact resistance, values of which could vary with time and/or position on the interface. This dependence is suggested to be important only for the thermal contact resistance less than 10^{-6} m²K/W [56].

Comparison between the splat morphologies from the numerical model and experiments for nickel impacting on a stainless steel substrate was done in [65]. When the contact resistance in the simulation was assumed to be $10^{-7} \text{ m}^2\text{K/W}$ the splat shape was close to the experiments performed on cold substrate (20°C). The splat morphology from the simulation with zero contact resistance (higher solidification rate), however, was close to the experiments for higher substrate temperatures (368°C). This was explained by slower solidification and thus greater particle spread for higher contact resistance case resulting in more liquid being in contact with the substrate at the initial stages of deformation and forming larger solidified layer on the substrate. Then, the rest of the liquid spread on the top of this layer and jetted out from its periphery. Closer inspection of the numerical results showed that the change of substrate temperature from 20°C to 368°C had no significant effect on the splat morphology.

According to [66], zirconia exhibits almost perfect disk-shaped splats on the hot substrates ($\sim 300^\circ\text{C}$) and extensively fingered splats on the cold substrates ($< 100^\circ\text{C}$). The thermal contact resistance of zirconia splats on a stainless steel substrate is of the order of $10^{-8} - 10^{-7} \text{ m}^2\text{K/W}$ for $T_s > 200^\circ\text{C}$ against $10^{-6} - 10^{-5} \text{ m}^2\text{K/W}$ for $T_s < 100^\circ\text{C}$.

2.5.4 Substrate surface temperature

The impacting droplets may assume a circular shape, or may splash and break up. It was found that the splat morphology differs significantly with the substrate temperature. In an effort to explain mechanism of droplet splashing, substrate surface temperature has gained the exceptional attendance in past few years [41], [45], [50], [51], [52], [67], [68],

[69], [70], [71], [72], [73]. Results indicate that breakup of thermal spray droplets on a smooth substrate occurs when substrate temperature is below a certain value. The temperature at which the splat shape becomes circular is referred to as transition temperature. Transition temperatures have been observed for a wide combination of substrate and droplet materials having very different melting points, thermal conductivities, thermal expansion coefficients, etc. The unusual aspect of this phenomenon is that it occurs at a relatively low substrate temperature, for most materials 100 – 400 °C, and the transition occurs over a narrow temperature range.

Many studies proposed some possible reasons for flattening splashing on a cold flat smooth substrate such as: rapid solidification on the bottom surface of a splat and jetting of the melt, desorption of adsorbates and condensates upon particle impact on the substrate surface, improved wettability at higher temperatures or severe oxidation of substrate surface. Most of the researchers tend towards the explanation by rapid solidification of the bottom of a splat before the spreading is completed to explain the change in splat morphology with the substrate temperature, for example [45], [47], [57], [59], [65], [66], [73].

It was believed that during the splat formation the solidification takes place after the spreading is completed due to the thermal contact resistance, undercooling and nucleation delay. It was shown that the nucleation delay is not very significant and the solidification time scale is on the same order of magnitude as the spreading time scale [57]. Also occurrence of substrate melting suggests that the molten splat - substrate interfacial thermal resistance on a hot substrate is not as large as assumed [74]. Therefore

solidification starts before the droplet kinetic energy is completely consumed.

On the cold substrate (below the transition temperature), the impacting particle spreads in the radial direction and localized solidification takes place. In [45], the time when all parts of the droplet in contact with the substrate freeze was estimated to be about $0.5\ \mu\text{s}$ after the impact. When the bottom layer of liquid in contact with the substrate solidifies, the remaining liquid jets out from the splat periphery. The surface of the solidified layer is not smooth and, therefore, the particle break-up is not symmetric. Fingers of liquid are formed around the splat, the tips of which detached to form small satellite droplets. When these droplets touch the substrate they are smeared out as they solidify. The result is the formation of solidified fingers around the bulk of the splat.

The higher substrate temperature (above the transition temperature) ensures that the temperature of the liquid splat during spreading on the substrate surface remains above the hypercooling temperature and therefore the splat remains in the liquid phase. Better contact and uniform heat conduction minimize localized solidification which is favorable for the formation of contiguous disk-shaped splats.

Another explanation for a change in the splat morphology with the substrate temperature is based on the contamination of the substrate surface by condensates and adsorbates [57], [68]. Clean surfaces energetically attract foreign species, which results in adsorption and condensation of water molecules and other substances. The amount of adsorbates on the solid surface depends on the surface temperature (desorption increases when the temperature rises), kind of adsorbates and surface energy. Multi-layer adsorption can take place and the adsorbed volume can be very high and possibly go to

infinity as the gas begins to liquefy. Evaporation of the adsorbates/condensates upon the impact of a hot droplet may cause the fragmentation during the splat formation.

The significance of this finding is that this can be universally applied for all the droplet and substrate material combinations. This hypothesis can explain the enhanced contact and observed higher cooling rates at the higher substrate temperatures. Also the problem that oxidation cannot explain fragmentation for low substrate temperature as well as for glass or oxide substrates does not take place.

Fig. 2.19: Calculated temperature at the interface of substrate-splat and at the surface of splat during its deposition (PSZ droplet with 400 K overheating on steel substrate). The interface temperature rise from ambient to over 2000 K in less than 1 μ s leads to a heating rate in the order of 10^9 K/s. This extremely fast temperature rise will explosively evaporate and expand the adsorbed gas/condensates [68].

The change in the splat morphology is postulated to result from formation of a gaseous cushion trapped beneath the splat due to the detachment and evaporation of the volatile substances upon the impact of a hot droplet (Fig. 2.19). The extremely high speed of spreading of an impacting droplet prevents some of the expanding gas from

escape (Fig. 2.20). The gas cushion will reduce the heat conduction from the splat and create instabilities in the spreading droplet, eventually causing splat fragmentation. The mechanism of fragmentation in the presence of a gas cushion could be analogous to film boiling, in which volatile liquid droplets are sprayed onto a heated substrate. A gas film is quickly formed between the substrate and the droplet. It may cause a poor contact between the droplet and the substrate, resulting in droplet fragmentation from jetting.

On the other hand, when the substrate is heated to approximately 200 - 400 °C, a typical temperature where contiguous splats are obtained, the substrate surface is relatively free of adsorbates and condensed volatiles and the effect of gas cushioning diminishes. Therefore, the splat - substrate contact area increases and the adhesion is improved [68]. Pores and voids are probably formed through the gas entrapment at the melt interface. At the higher temperatures, the substrate is relatively free of volatiles and the pores do not form.

Fig. 2.20: Droplet spreading on the substrate with and without condensates/adsorbates [68].

2.5.5 Splat solidification and microstructure

There is a little knowledge about the microscopic heat transfer for the cases of large temperature difference of over 1000 K, though this heat transfer critically influences microstructure formation of the deposited layers. The cooling of the splat on the substrate surface determines the extent of undercooling, the cooling rate, crystal growth and the formation of metastable or amorphous phases [56], [66].

During rapid quenching significant undercooling can occur, nucleation can be suppressed and once released it results in fast solidification and competitive growth of alternate phases. The results of experimental investigations on the crystallization of small metallic drops showed undercooling up to 200 °C [60]. Undercooling for zirconia splats on stainless steel substrate preheated to 450 °C was estimated to be about 700 °C [226].

Fig. 2.21: Schematic of temperature gradients vs. interface velocity showing regions of different solidification microstructure [61].

Different solidification microstructure as a function of the temperature gradient and the solid-liquid interface velocity is shown in Fig. 2.21. The interface velocity depends

on the extent of undercooling and also on the interfacial heat transfer coefficient, which describes the quality of the interfacial contact between the splat and the substrate. At medium interface velocities the interface is unstable due to constitutional undercooling leading to cellular or, in case of further front velocity or the temperature gradient decrease, to dendritic solidification. The constitutional undercooling results from inability of the solute atoms to diffuse away from the moving solid-liquid interface quickly enough to maintain uniform liquid composition. A reverse transition from cells to a planar front is observed at high interface velocities and is essentially independent of the temperature gradient. Above a certain temperature gradient the planar front is always stable [61].

The microstructure of the splat depends on the cooling rate of the flattened particle. The increase in particle cooling rate (e.g. due to the increase in particle impact velocity, degree of flattening, lower thermal contact resistance, substrate temperature higher than the transition temperature) results in finer grains or columns within splats. Typical values of grain sizes are between 50 and 200 nm. For substrate temperature higher than the transition temperature, the contact between splat and substrate is excellent and the grain size within splat is 2 to 4 times smaller than in the case for substrate temperature below the transition temperature, which case corresponds to smaller contact area between splat and substrate [62].

It might be expected that intimate contact between the substrate and impinging droplet would favour heterogeneous nucleation. In contrast, the small volume of material and large cooling rate would tend to increase the undercooling required for nucleation.

According to [168] the undercooling during the splat quenching lies in the range of $(0.1-0.2) T_m$, i.e. approaching the conditions for homogeneous nucleation usually taken as $0.2 T_m$. Nucleated crystals will grow into a highly undercooled melt at a growth rate which will not be limited by the rate of heat removal, unless the temperature increases to the equilibrium melting point by recalescence. An increase in temperature of the liquid droplet, produced by release of the heat of fusion during rapid crystal growth, would tend to suppress further nucleation because of the large temperature dependence of nucleation rate, and columnar crystal growth from the interface into the droplet would be expected. If, however, the rate of heat loss by conduction through the substrate interface was greater than the rate of heat liberated by crystallization, the temperature would continue to decrease, the nucleation rate would increase and crystallization would be controlled by nucleation to give a fine equiaxed microstructure. The crystal growth rate is therefore an important factor in determining the microstructure produced in sprayed coatings but the heat extraction rate is so great that the time interval for solidification will be extremely small whether it is controlled by growth or nucleation.

Two different grain morphologies were observed inside the splat after solidification. Fig. 2.22 shows a scheme of the planar morphology of a solidified particle. In the central core region, where the particle first comes into contact with the surface, heat is extracted through the substrate, and the solid - liquid interface moves away from the substrate. However, in the peripheral areas, heat is not extracted through the substrate but rather back through the core region. This is indicated by the radially elongated grains, which propagate from the core and terminate at the rim. Furthermore, the virtually defect

free and regularly patterned grains suggest that these thin regions are not in full contact with the substrate [3], [63], [66].

Fig. 2.22: Two different morphologies revealed in splat after solidification [3].

The solidification of ceramic YSZ splats on different substrates was studied in [225], [226], [227]. YSZ splats on preheated polished stainless steel substrates revealed the typical columnar grain microstructure. The columnar grains were straight, perpendicular to the substrate, and very narrow having widths ranging from 30 to 100 nm. During spreading of the droplet, excellent physical contact was established between the liquid and the hot substrate, which enabled rapid heat extraction from the liquid. After spreading of the ceramic liquid droplet was completed, the thin liquid layer was undercooled enough so that copious heterogeneous nucleation started at the substrate surface. The nucleated grains first grew laterally to cover the substrate surface, and then a stable set of narrow columnar grains continued to solidify, with a planar solid-liquid interface through the thickness of the splat in the direction of the heat flow. The grains were not perfectly parallel-sided but the growing solid grains

competed with each other for the addition of atoms.

Cooling rate was lower on preheated substrates covered with polished bond coat or cold substrates resulting in smaller undercooling of the molten ceramic, and therefore fewer nucleation sites for heterogeneous nucleation at the interface of splat and substrate. The primary manifestation of the low cooling rate was the occurrence of equiaxed grains. Heat developed at the beginning of solidification (recalescence) may not be extracted from the region at a fast enough rate, and the velocity of the solidification front is thus slowed down or even stopped. This allows time for a new nucleation process within the molten puddle to start.

2.6 Coating build-up

The thermal spray coatings are built-up by successive impacts of particles on the substrate surface or previously deposited layers. The particles can be fully or partially melted or solid at the moment of impact. The solid particles will rebound or remain weakly connected with the rest of the coating, reducing its toughness. That is why the careful optimization of spray parameters should lead to the elimination of such particles. The molten particles deform to lamellae and solidify, giving columnar or fine-grained equiaxed crystals [1]. The plasma sprayed coatings exhibit characteristic lamellar microstructure which gives rise to unique properties of the deposits. These include anisotropy, the presence of pores and cracks, lower density, thermal and electrical conductivity, strength and modulus (compared to their bulk counterparts) and residual stress. These properties then determine the coating performance and lifetime in service.

The coating microstructure and the properties are controlled by the splat formation, layering and mutual contact between the splats, and depend on number of characteristics of both substrate and impacting droplet. Some of these characteristics are listed in the introduction to chapter 2.5 [44], [45], [73].

During plasma spraying, the torch moves over the substrate surface and the first layer is formed. The layer formation depends strongly on the time between two successive impacts [41]. After a droplet impact on the substrate, the resulting splat undergoes a very rapid cooling to level generally below its melting temperature. This cooling is followed by periodic reheating by the subsequent incoming particles. This “heat impact” decreases quickly as the splat is covered by other lamella. The thermal history during splat layering is closely linked to the number of splats that impact at the same location during the torch movement. It depends on the powder feed rate, the deposition efficiency and relative torch - substrate velocity. When the layer is made up of a few splats, temperature drop within them is very fast, while when the layer is thick (more than about 30 splats depending on the splat thermal properties) important temperature gradients can develop, resulting in a variation of coating structure with thickness. The extreme case is achieved with very thick passes (100 – 200 μm thick) of materials with low thermal conductivity. In that case, the sprayed droplet can impact on still liquid lamellae and a columnar growth is achieved through the whole layer. It results in coatings similar to those obtained by electron-beam physical vapor deposition (EB PVD) [76].

The torch returns after some time to the same spot. Meanwhile the layer surface is submitted to the action of the surrounding environment, such as oxidation (for oxidizable

materials) and cooling. During the spraying of the layer the torch heats the previously deposited coating. Additional heat fluxes come from particle solidification and their cooling down to the actual temperature. The cooling leads to the generation of residual stresses and, eventually, cracking.

Influence of the substrate temperature on a change in the splat morphology has been already discussed in the previous chapter (2.5.4). The substrate temperature affects splat morphology through the change in interface nature, surface chemistry, solidification behavior, wetting and contact of the molten droplet with the substrate. The splat morphology plays an important role in the nature of the deposit build-up process and consequently affects the microstructure and properties of the sprayed materials. For example, in the case of PSZ, the transition temperature for the splat was observed to be in the range of (200 - 250) °C. Reduced splashing and debris content, enhanced adhesion/cohesion and coating integrity, porosity reduction, increase in thermal diffusivity and erosion resistance improvement were observed in samples prepared on hot substrates [57].

Besides, there is a strong thermal interaction between the droplet and the substrate leading to dramatic increase in the interface and overall substrate temperature. Possible substrate melting during such interaction results in metallurgical bonding between the impinging particle and the substrate surface and thus provides substantial contribution towards coating adhesion strength. If the substrate starts to melt, the maximum melting depth achieved is an important parameter for the bonding quality. On the other hand, the substrate melting can cause unwanted substrate damage and change of chemistry [74].

However, bonding of the plasma sprayed coatings to the substrate (adhesion) has predominantly character of a mechanical interlocking with the substrate unevenness. Bonding between the individual splats is called cohesion and is strongly dependant upon the contact area at the splat - splat interface. The areas of contact correspond to (20 - 30) % of the lamella total area [1]. It can be estimated by comparing the thermal diffusivity of the deposits with that of corresponding sintered material.

It was shown that preheating the substrate without significant oxidation produces higher values of the coating adhesion/cohesion. The phenomenon is probably linked to the difference in the splat morphology with the substrate temperature. The adhesion/cohesion can also be increased by a higher particle impact velocity for a given substrate temperature higher than the transition temperature [65]. Improved adhesion at higher temperature substrates is supported by the observation of crack patterns in the splats, which is a mean of stress relief [68], [73].

The residual stress is an important factor influencing the integrity of the deposit - substrate system as well as its performance. In the plasma spray process, the residual stress originates from the large temperature differences experienced during the process. The resulting stresses can be attributed to the following phenomena [1], [44], [75]:

- Quenching stress. When the molten particles strike the substrate, they are rapidly quenched (10^4 to 10^6 K/s), while their contraction is restricted by adherence to the substrate. Since particles are forced to remain in a stretched condition they experience a tensile stress, commonly referred to as quenching stress. This stress

is often high enough to cause micro-cracking in brittle materials.

- Stress generated during deposition of one pass of the torch, caused by reheating of already solidified splat by subsequently arriving particles.
- Thermal stress. During the deposition, the substrate is usually at some elevated temperature. Cooling to room temperature causes thermal mismatch stress to develop due to the difference in thermal expansion between the coating and the substrate. Depending on the sign of this difference and the deposition temperature, the evolution of thermal stress can be tensile or compressive (Fig. 2.23).
- Phase transformation stress. Stress generated in the sprayed coating or substrate if phase transformation takes place during processing (spraying or post spraying treatment).

The residual stress of the plasma sprayed coating increases with coating thickness. In case of ceramic coatings at high deposition rates, the residual stress changes from compressive to tensile beyond a critical thickness. On the other hand, for high heat conductivity materials, the residual stress remains in a compressive state.

For ceramics the thermal stress is dominant, quenching stress is usually small, since it is reduced by cracking in the brittle ceramic, and the difference in thermal expansion is more pronounced [73]. The thermal stress becomes also more significant with increasing substrate temperature, since the thermal expansion of the ceramic is smaller than that of the substrate (thermal expansion coefficient of the YSZ is about half of that of the bond

coat in TBC systems). When the coating - substrate composite cools after deposition, a residual stress component arises, which is always compressive because the coating is not contracting as much as the substrate. A hotter substrate will result in a larger compressive stress [75].

Fig. 2.23: Generation of a thermal residual stress in a ceramic coating deposited on a metallic substrate (coefficient of thermal expansion of a ceramic coating is lower than that of a substrate).

The stress has also important implications for the coating microstructure. Residual compressive stress is reported to be quite detrimental, because there is an induced tensile stress perpendicular to the plane of the coating, which causes delaminations between the coating layers, parallel to the coating plane. At lower substrate temperatures, the tensile stress is higher, but this stress remains in the plane of the coating and tends to induce vertical, perpendicular to the coating plane, micro-cracking (for brittle materials) during deposition. A higher density of such cracks provides a toughening effect, because they arrest cracks that are propagating through the plane of the coating [73], [75].

Another important substrate parameter is substrate roughness. The effect of the substrate roughness on the flattening, splashing and cooling of the droplets depends on the relation of dimensions of unevenness with respect to a splat size. As a general rule, the splat thickness increases and the flattening degree decreases with the substrate roughness and its cooling rate decreases. Therefore, splashing is enhanced by both the longer time in molten state and the rough surface. Compared to smooth substrates, more splashing with fingered splats and satellite droplets is observed on rough substrates. Also, the roughness of the substrate influences, to a degree, the coating surface roughness. The coating roughness increases with the powder particle size and decreases if the particle velocity and temperature at the moment of impact are greater [1], [41], [45], [46], [65].

2.7 Zirconia and alumina – materials in plasma spray

2.7.1 Zirconium dioxide – zirconia, ZrO_2

Zirconium dioxide (ZrO_2) or zirconia is a material of high engineering importance and scientific interest. Pure zirconium dioxide is a polymorphic material and exhibits three well-defined polymorphs: a monoclinic phase, a tetragonal phase, and a cubic phase (see Fig. 2.24 and Table 3). The monoclinic phase is a low temperature phase, stable to 1 170 °C, at which temperature it changes reversibly to the tetragonal phase, which, in turn, is stable to 2 370 °C. Above that temperature the cubic phase becomes stable up to the melting point of 2 680 °C. It is most likely that very little or no volume change occurs during the $c-t$ transformation. The t -lattice can be regarded as the slightly distorted cubic

one, whereas the t - m inversion is much more dramatic: the number of O-atoms coordinated to zirconium changes from 8 to 7. The t - m transformation involves a spontaneous shear deformation and a volume increase (tetragonal phase is denser than monoclinic phase), which is destructive for most zirconia-ware [85].

Fig. 2.24: Three polymorphs of zirconia [205].

Table 3: Lattice parameters of three zirconia polymorphs.

Lattice	a (Å)	b (Å)	c (Å)	alpha	beta	gamma	Ref.
Cubic	5.09	5.09	5.09	90	90	90	[111]
Tetragonal	3.64	3.64	5.27	90	90	90	[112]
Monoclinic	5.169	5.232	5.341	90	99.25	90	[113]

Polymorphic transformations can be displacive or reconstructive. The reconstructive transformations often are very sluggish and can lead to metastable phases, but the displacive transformations generally are rapid and reversible over a small temperature range [114].

Displacive transformation involves distortion of the structure, such as a change in bond angles, but does not include breaking of bonds. It typically occurs rapidly at a well-defined temperature and is reversible. The martensite transformation in metals is

a displacive transformation. So also is the tetragonal-monoclinic ZrO_2 transformation.

Reconstructive transformation is another type of transformation. Bonds are broken and a new structure is formed. Much more energy is required for this type of transformation than for a displacive transformation. The rate of reconstructive transformation is low, so the high-temperature structure can usually be retained at low temperature by rapid cooling through the transformation temperature.

The displacive transformations generally involve a significant volume change, such as for the tetragonal-monoclinic ZrO_2 transformation. It is possible to prevent a polymorphic transformation from occurring by restraining the volume change and thus achieving a metastable phase. Pure ZrO_2 goes through the transformation between tetragonal and monoclinic crystal forms in the temperature range from 800 to 1 100 °C. During cooling this transformation involves several percent volume increase. In order to restrain the volume increase and retain the tetragonal phase metastably to room temperature, following assumptions must be fulfilled; (i) the ZrO_2 particles are small enough, (ii) a controlled amount of Y_2O_3 (or one of several other specific oxides) is added as a stabilizer, and (iii) the surrounding microstructure is strong enough. The resulting material has remarkable mechanical properties, including unusually high toughness and strength for a ceramic material (Table 4). The mechanism of the toughening involves controlled transformation of the metastable tetragonal phase to the stable monoclinic phase and is referred to as transformation toughening.

Transformation-toughened materials owe their very high toughness to the stress-induced transformation of the metastable tetragonal phase in the vicinity of a propagating

crack. To understand the phenomenon, it is useful to refer to Fig. 2.25. With proper chemical additions and heat treatments, a microstructure can be achieved during cooling that consists of lens-shaped “precipitates” of tetragonal zirconia in cubic grains of zirconia. Normally, the tetragonal material would transform to the monoclinic form during cooling, but it must expand to do so. The high strength of the surrounding cubic zirconia prevents this expansion, so the tetragonal form is retained all the way down to room temperature. As a result, each tetragonal zirconia precipitate is under the stress and full of energy that wants to be released. If, for any reason, constraint is lost, the transformation that is accompanied by a relatively large volume expansion or dilatation ($\sim 4\%$) and shear strain ($\sim 7\%$) is induced.

Fig. 2.25: Transformation zone around crack tip [88].

In transformation toughening, the approaching crack front, being a free surface, is the catalyst that triggers the transformation. When a stress is applied to the zirconia and a crack tries to propagate, the metastable tetragonal zirconia grains adjacent to the crack tip expand and transform to the stable monoclinic crystal form. The transformation causes the volume increase, which places the crack in compression and stops it from

propagating. Extra energy (tensile stress) is now required to extend the crack through that compressive zone. The result is a ceramic that is very tough and strong and that has been appropriately referred to as “ceramic steel” [85], [86], [87], [88], [108], [109].

Fig. 2.26: Fracture toughness versus composition for transformation toughened ZrO_2 -based materials [88].

Pure ZrO_2 does not have the transformation-toughening behavior. Additives are required to stabilize such behavior. These additives are CaO , MgO , Y_2O_3 , CeO_2 , and rare earth oxides. Too much addition fully stabilizes ZrO_2 in a cubic crystal structure, which also does not have the transformation-toughening behavior because it does not go through the tetragonal-to-monoclinic transformation. Toughening requires the presence of the metastable tetragonal state. The range of addition to achieve the metastable tetragonal state and toughening is shown for various ZrO_2 -based compositions in Fig. 2.26. The peak of the curve for each material corresponds to the maximum tetragonal content. Monoclinic content increases to the left of the peak and cubic to the right of

the peak, each resulting in a decrease in toughness and strength. Note that the composition zones for achieving the peak toughness are relatively narrow [88].

Table 4: Selected properties of ZrO₂ and Al₂O₃ ceramics.

Properties	Al ₂ O ₃ 99.9 %, alpha phase	ZrO ₂	
		Monoclinic	Tetragonal
Density (kg/m ³)	3890	5600	6100
Molecular weight (g/mol)	101.961	123.22	
Hardness, Vickers	1365-2000	1300	
Tensile strength (MPa)	300	248	
Modulus of elasticity (GPa)	370	160	205
Flexural (bending) strength (MPa)	379	900	1300
Compressive yield strength (MPa)	2100-3000	2500	3900
Poisson ratio	0.22	0.32	
Fracture toughness (MPa.m ^{1/2})	3.5-4	8-13	
Electrical resistivity (Ohm.m)	10 ¹²	10 ¹¹	
Dielectric constant	9.9	26	
Heat of fusion (J/kg)	1.075x10 ⁶	7.08x10 ⁶	
CTE, linear 20°C (µm/m.°C)	7.4-8.2	7-10.5	12
Specific heat capacity (J/kg.K)	1300	9628	
Thermal conductivity (W/m.K)	18-30	2.2	2.3
at elevated temperature	6.3	2.3	
Melting point (°C)	2054	2680	

Specific terminology has evolved to describe the different transformation-toughened ZrO₂ materials based on additives and microstructure. The material with tetragonal precipitates is referred to as partially stabilized zirconia, or simply PSZ. The additive is normally identified by a prefix; i.e., Ca-PSZ, Mg-PSZ, and Y-PSZ. In these materials the cubic phase content is lower than in those totally stabilized. The cubic phase is then heat-treated to form coherent tetragonal precipitates. The heat treatment is such as to keep the precipitates small enough so they do not spontaneously transform within the cubic zirconia matrix but only as a result of stress. If enough stabilizer is added, the material contains only the cubic phase and is referred to as fully stabilized zirconia.

The $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{CeO}_2\text{-ZrO}_2$ materials with essentially all tetragonal phase are called tetragonal zirconia polycrystals; i.e., Y-TZP and Ce-TZP. Zirconia-toughened ceramics (ZTC) consist of tetragonal or monoclinic zirconia particles finely dispersed in other ceramic matrices such as alumina, mullite, and spinel.

Fig. 2.27: Phase diagram of the ZrO_2 -rich region of the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system. M – monoclinic phase, C – cubic phase, T – tetragonal phase, L – liquid, t' – nontransformable tetragonal phase [108].

The most common zirconia addition is yttria. At low yttria content an initially pure white color of both substances becomes yellow after firing. At higher yttria content, a white color reappears. The best performance in thermal barrier coatings is currently achieved by using ZrO_2 partially stabilized by 6 - 8 wt.% (equivalent to 3.4 - 4.5 mol.%) of Y_2O_3 . Rapidly quenched zirconia of this composition from the high-temperature liquid or cubic region (see phase diagram in Fig. 2.27) yields the 'non-transformable' tetragonal t' phase which, although metastable, can withstand repeated cycles to temperatures up to

1100 °C without decomposition into the equilibrium tetragonal and cubic phases. The tetragonal t' phase is thought to be fundamentally the same tetragonal polymorph as the equilibrium “low-stabilizer content” tetragonal phase, which occurs at 2 - 3 mol.% Y_2O_3 , but to differ in physical microstructure, with the t' phase being distinguishable by its anti-phase domain boundaries and numerous twins [110].

2.7.2 Aluminium oxide – alumina, Al_2O_3

Aluminium oxide (Al_2O_3) or alumina is the most cost effective and widely used ceramic material. Raw materials from which this high performance technical grade ceramic is made are readily available and reasonably priced. As a naturally occurring oxide component, alumina is abundant, comprising about 15 wt.% of the earth's crust [123]. With an excellent combination of properties, such as chemical inertness, hardness, electrical resistivity, and high-temperature strength, it is no surprise that alumina has a very wide range of applications. Its applications, ranging from biological implants to abrasives, insulators, and refractories, include spark plugs, tap washers, pump seals, electronic substrates, grinding media, abrasion resistant tiles, cutting tools, hip-joints, body armour, laboratory ware and wear parts for the textile and paper industries. Very large tonnages are also used in the manufacture of monolithic and brick refractories.

The structures of the aluminium oxides are based on aluminium ions surrounded in six-fold coordination by oxygen. These coordination octahedra are arrayed in either hexagonal or cubic packing sequence. Consistent with an internationally accepted crystallographic nomenclature, the prefix α should be used to designate the hexagonally

packed structures; for example corundum. For the cubically packed structures the prefix γ should be used [124]. Lattice parameters for hexagonal and cubic alumina structures are listed in Table 5. Thermally stable α -alumina is sometimes referred to be rhombohedral. Rhombohedral configuration has a hexagonal nature of its lattice, and the relationship between rhombohedral crystals and ordinary trigonal or hexagonal crystals, is often represented as hexagonal lattice with two interior points equally spaced along a diagonal.

Table 5: Lattice parameters of hexagonal and cubic alumina polymorphs.

Lattice	a (Å)	b (Å)	c (Å)	alpha	beta	gamma	Ref.
Hexagonal	4.754	4.754	12.99	90	90	120	[121]
Cubic	7.887	7.887	7.887	90	90	90	[122]

Fig. 2.28: Schematic picture of the hexagonal close packed structure and α -alumina crystal structure.

Pure, stoichiometrically defined aluminium oxide occurs in the crystalline modification corundum, α - Al_2O_3 . Corundum is the only thermodynamically stable form of aluminium oxide. Corundum is very hard, its hardness is exceeded only by that of

a diamond and a few synthetic compounds having the diamond structure. Alpha Al_2O_3 crystallizes in the hexagonal-rhombohedral system. The lattice represents a hexagonal closest packing of oxygen ions. Each Al ion is octahedrally coordinated by six oxygens (Fig. 2.28). It is the close packing of the aluminium and oxygen atoms within this structure that leads to its good mechanical and thermal properties.

Seven crystallographic phases that arise during the heat treatment have been reported for aluminium oxide. Yet there appears to be no evidence that any of the others are thermodynamically stable relative to $\alpha\text{-Al}_2\text{O}_3$ [123]. These polymorphs are therefore to be regarded as metastable, achieving true stability relative to corundum only to extent that they can incorporate other oxides or elements into their structure. Many of these structures are derived from a cubic close-packed lattice, whereas corundum is hexagonally close-packed. The transformation sequence with time along the alumina polymorphs at 750 °C to 1 250 °C is $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$.

Alpha alumina varies little in stoichiometry with regard to aluminium and oxygen. An equilibrium diagram for the system Al- Al_2O_3 is shown in Fig. 2.29. There are no phases richer in oxygen than Al_2O_3 . Alumina melts congruently and its melting temperature is 2 054°C. The reaction of aluminium metal with oxygen to form alumina is accompanied by a substantial reduction in Gibbs energy. The thermodynamic stability of Al_2O_3 relative to its constituent elements, in terms of free energies per atom of metal oxidized, is quite high as compared to that of other important oxides. This high degree of thermodynamic stabilization is in part responsible for many of the useful properties of alumina [124] (Table 4).

Fig. 2.29: Equilibrium diagram for the system Al-Al₂O₃ [124].

Like many other ceramics, alumina is not only fabricated and used in its pure, single-phase configuration Al₂O₃, but there exists a wide series of material compositions which start from Al₂O₃ as a base material and contain one or more other ceramic or even metallic phases. Alumina can be considered a typical representative of the group of structural ceramics. These ceramics are intended particularly to serve as structural parts subjected to mechanical loads, in many cases at high temperatures [126]. Continuous solid solutions of corundum with Cr₂O₃ can be made, and extensive, but partial solid solutions occur with Fe₂O₃ and Ga₂O₃. Alumina reacts with most other oxides to form one or more intermediate binary compounds; the resulting aluminates include members of spinel, beta alumina, perovskite, tridymite, and garnet structural families. The composition of the ceramic body can be changed to enhance particular desirable

material characteristics. An example would be additions of chrome oxide or manganese oxide to improve hardness and change color. Alumina can also achieve transformation toughening by addition of PSZ (partially stabilized zirconia) particles. Alumina is strong enough to prevent the PSZ particles from transforming during cooling and no interaction between materials occur. Addition of 15 – 25 % of sufficiently small particles of zirconia to alumina results in toughness and strength nearly equivalent to that of the pure transformation toughened zirconia, but the alumina is cheaper and much lighter in weight.

2.7.3 Plasma spray applications of alumina and zirconia coatings

Alumina and zirconia, due to their properties, are one of the most extensively used ceramic materials in a plasma spray technology for preparation of protective coatings. A thin surface layer of ceramic deposited on metal imparts favorable ceramic characteristics, such as corrosion resistance, wear or thermal resistance, while retaining the durability and structural benefits of the metal.

Zirconia-based coatings are attractive due to their low thermal conductivity, large coefficient of thermal expansion as compared to ceramic materials, good microstructure stability, high mechanical properties, good thermal shock resistance and oxidation resistance. The coatings of zirconia alloys are mostly used in high-temperature environments as the thermal barrier coatings (TBC). In the aerospace industry, the TBCs are used primarily to protect austenitic superalloy blades and vanes of gas turbine engines, turbine shrouds and combustor cans. The automotive industry uses these coatings to protect components such as pistons, valves, and intake and exhaust ports

against wear and corrosion, particularly in diesel engines [116].

Thermal barrier coating is a multilayer system consisting of a ceramic topcoat, a metallic bond coat and a superalloy substrate. The structure of ZrO_2 changes from monoclinic to tetragonal when heated above 1 000 °C. The accompanying volume change can result in severe spalling of the ceramic layer. Therefore, PSZ coatings made from ZrO_2 alloyed with stabilizing oxides such as Y_2O_3 (most common), CeO_2 and MgO are used. The purpose of the bond coat, typically a MCrAlY ($\text{M} = \text{Ni}, \text{Co}$) alloy, is to improve the adherence of the ceramic coating to the substrate and it also acts as an oxidation barrier for the substrate, which typically is a Ni or Co based superalloy [115]. The smooth transition of the bond coat's coefficient of thermal expansion between that of the base metal and that of the TBCs ($\text{Y}_2\text{O}_3\text{-ZrO}_2$) has been believed to reduce the interfacial thermal stresses produced during coating deposition and service thermal cycling [76].

Thermal barrier coatings do not only reduce the metal substrate temperature but also wear damage, oxidation or hot corrosion by molten salts and corrosive gases. They also increase the lifetime of components by increasing the turbine blade cooling efficiency. To increase the fuel efficiency and to reduce the levels of hydrocarbons in engine exhaust gases, the combustion temperatures need to be raised further. Development of thick TBC (up to 3 mm) with improved mechanical properties is critical to operation at a higher combustion temperature. It has been estimated that a 50 % reduction in thermal conductivity will reduce the alloy temperature by about 55 °C. This may not seem a large change, but it actually corresponds to the increase in high

temperature capability achieved over the last ~20 years by developments in single-crystal Ni-based superalloys [117]. Nowadays, the main turbine-producing manufacturers provide an initial gas temperature level of (960 – 1 100) °C for basic service and (1 065 – 1 300) °C for peak service. In military aircraft turbines, the temperature of the gas rises to 1 600+ °C and for commercial aircraft up to 1 500+ °C. The maximum operational temperatures for refractory Ni-base superalloys used for blade production reach (850 – 1 100) °C (for single crystal) [76].

There are other severe constraints, except the primary function as a thermal barrier, TBCs have to meet when working in critical thermomechanical environments [117]. For example, to withstand the thermal expansion stresses arising during cooling and heating. This is ensured by plasma sprayed coating porosity. Typical air plasma sprayed coatings usually have porosity of (10 - 20) %. Coating material must not undergo phase transformations when it is repeatedly loaded between room and service temperature. Such transformations are usually accompanied by volume changes, which detract from the strain compatibility and reversibility of the coating and, hence, its ability to withstand repeated thermal cycling. TBC materials must also be able to resist erosion or, for air-breathing engines, prolonged service at high temperatures in an oxidizing atmosphere. The coating material has to be thermodynamically compatible with the thermally grown oxide (TGO), developed between the bond coat and topcoat in service at high temperatures. Currently used bond coats mostly form slow-growing Al_2O_3 , under oxidative conditions typical for operation (Al_2O_3 has the lowest oxygen diffusivity of the common oxides).

Several failure mechanisms which can participate, separately or in combination, in TBC system malfunction are [76]:

- erosion loss
- large differences in coefficient of thermal expansion of the ceramic insulating layer, the metallic bond coat and the substrate alloy
- oxidation of the bond coat
- sintering within the ceramics
- phase changes in the thermally grown oxide, bond coat and ceramic layer
- creep of the bond coat or substrate
- and accumulation of micro-cracking during thermal cycling

The primary failure mechanism of TBCs is delamination of the ceramic thermal barrier topcoat from the bond coat. After delamination, the unprotected part of the component is exposed to oxidation, and even local melting can occur at high gas temperatures, leading to the failure of the component. Coating delamination is probably the result of cyclic thermal and mechanical loading experienced in service together with the increase of TGO thickness in the vicinity of large-scale interfacial imperfections. Growth of TGO is accompanied by an in-plane compressive stress development that causes an out-of-plane stress rise, particularly at the interface which can lead to the delamination of the coating [118], [119].

Plasma sprayed alumina-based coatings have been widely used to protect surfaces against various types of adverse environments involving high temperatures, wear.
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corrosion, erosion as well as to provide electrical insulation and chemically unreactive surfaces [129], [130], [131], [132]. Alumina is often used in combination with titania in most applications. The use of the composite in preference to pure aluminium oxide has certain advantages. Titanium oxide has a lower melting point and effectively binds alumina grains leading to higher density and wear resistance. Another candidate material to produce alumina based coatings is magnesia due to its high electrical and radiation resistivity [133].

Aside from titania and magnesia, alumina can be mixed also with zirconia to improve characteristics of traditional thermal barrier coatings [134], [135]. It was reported that deposits of ZrO_2 and Al_2O_3 alternating layers exhibited the reduction of oxygen diffusion through the deposits. The development of an oxygen diffusion barrier in the TBC, which reduces the thermally grown oxide layer at the bond coat - zirconia interface, is critical for improving turbine blade performance. In [119], it was shown that a thin plasma sprayed layer of Al_2O_3 applied between the top coat and bond coat improved oxidation resistance and reduced the interfacial thermal stress due to the thermal expansion mismatch in the TBC system. The plasma sprayed alumina/zirconia alternating coatings showed an increase in temperature drop as compared to single-layered YSZ coatings. The thermal shock resistance of the laminated coatings was also found to be far superior to that of single bulk coatings. Addition of alumina to the zirconia layers was effective in reducing the sources of residual stresses and reduced the formation of cracks. No significant decrease in thermal conductivity was observed, which suggests relatively small influence of interlayer interfaces on heat

transfer and thus good bonding between the Al_2O_3 and YSZ layers. The values of thermal conductivity/diffusivity measured at different temperatures were between those of pure alumina and zirconia coatings [116], [136], [137].

Thermal barrier coatings were also prepared using the solution precursor plasma spray (SPPS) deposition technique. In the SPPS method a liquid-precursor feedstock is used instead of the conventional powder feedstock used in atmospheric plasma spray. SPPS TBC has a unique microstructure with vertical cracks in a porous matrix and an absence of coarse splats that are always present in APS. The matrix of the coating consists of ultra-fine splats and unmelted particles. The unmelted particles, the porosity and especially the cracks through the coating thickness all impart strain tolerance to the TBC, while the porosity helps to reduce the thermal conductivity. The vertical cracks with spacing less than the coating thickness result in low stress in these coatings. For a coating with lower residual stress, the minimum crack size for buckling initiation is larger than that needed for a coating with higher residual stress. This means that SPPS coating can tolerate a crack of sufficient size that can initiate buckling in the APS coating. The longer time needed to develop a crack of a certain size and the capability of SPPS coating to tolerate a larger crack lead to the durability of the SPPS TBC to be more than 2.5 times of that of the conventional TBC. The thermal conductivity was found to be independent of the temperature, with value of about 1.3 W/m.K which is in the range of 0.8 - 1.7 W/m.K for conventional plasma spray TBCs. Also, 4 mm thick SPPS coatings were deposited, having porosity of about 22 % and indentation toughness over five times that of the reference APS coatings [140], [141], [142], [143], [144].

3. MATERIALS AND EXPERIMENTAL SETUP

In this chapter, descriptions of zirconia and alumina powders used in this experiment, basic characterization of the substrate material used for splat and coating depositions, the plasma spray setup with attached SprayWatch monitor system and some special experimental techniques (laser flash method, electrochemical impedance spectroscopy) are given.

3.1 Yttria stabilized zirconia (YSZ) powder

Zirconia powder used in this study was stabilized with 8 wt.% of yttria. The powder was obtained from Praxair Surface Technologies (Al-1075) in an agglomerated and sintered form.

Fig. 3.1: SEM pictures of as-received YSZ powder particles: surface and cross-section.

A scanning electron microscopy (SEM) analysis of powder particles revealed their spherical shape (Fig. 3.1). In the SEM pictures it can be seen, that some of the particles are broken into smaller fractions and a lot of small satellite particles are attached to larger

ones. Particle debris is of irregular shapes. All these can lower the powder flow characteristics. The YSZ particles after agglomeration and sintering from smaller particulates contain inherent porosity which can, together with the inter-particle boundaries, reduce a heat transfer inside the particle, and thus its melting, when propelled in the plasma jet. These pores can be seen on the particle surface during high magnification SEM observations.

Fig. 3.2: Particle size distributions for original YSZ powder and powders after sieving to different size ranges.

The particle size range of as-recieved powder was measured by a laser light scattering analyser Analysette 22 from Fritsch. An arithmetic mean diameter was measured to be about 45 μm . To ensure more uniform heating and momentum transfer, and hence more uniform particle velocity and temperature distributions, during plasma

spray, powder was sieved to obtain smaller particle size intervals. Two lots of YSZ powder were used in this experiment with the different particle size ranges; i.e., (20 - 45) μm and (45 - 75) μm . The particle size distributions are shown in Fig. 3.2 together with the respective cumulative functions. According to the information provided by a supplier, powder contains 27 % of the zirconia monoclinic phase and less than 1% of bcc yttria and other non-zirconia phases. Other zirconia phases make the balance. Phase composition of raw powder was investigated by Raman spectroscopy and X-ray diffraction to be compared with powders after plasma spray and will be discussed in sections 5.4.3 and 5.4.4.

3.2 Aluminium oxide (alumina) powder

Alumina powder used in this study is a pure aluminium oxide purchased from Praxair Surface Technologies (ALO-101) in a crushed form. As it can be seen from SEM pictures in Fig. 3.3 particles of alumina powder have irregular shapes with sharp edges. This lessens the powder flowability and can lead to a choking of powder in the feed hose of the plasma spray system. As compared to the YSZ powder, alumina particles are compact and do not contain any porosity. Their irregular shape balances this specious advantage for better heat transfer in alumina particles. A heat and a momentum transfers from plasma towards the powder particles are subjected to the orientation of irregular particles in the plasma jet, which designates the effective cross section for such transfers.

The alumina powder particle size range was measured by a laser light scattering analyser Analysette 22. In order to obtain a narrow particle size range which could be

Fig. 3.3: SEM pictures of as-received alumina powder particles: surface and cross-section.

Fig. 3.4: Particle size distributions and respective cumulative functions of as-recieved and sieved alumina powders.

compared to that of zirconia, powder was sieved to the particle size range of (20 -45) μm .

The actual particle size distributions and respective cumulative functions of as-recieved

and sieved alumina powders are shown in Fig. 3.4. From this figure it seems that there is not a big difference in the particle size between as-received and sieved powder. However, the particle size measurement and sieving process itself are, to some extent, influenced by the particle irregular shape.

According to the information provided by a supplier, powder contains at least 99 % of aluminium oxide. Traces of sodium oxide, calcium oxide or ferric oxide can be found. Raw powder contains the alpha alumina phase only as it was confirmed by X-ray diffraction and Raman spectroscopy (see sections 5.4.3 and 5.4.4).

3.3 Substrates – 316L stainless steel

Substrates from stainless steel, 316L, were used for the splat and coating depositions in this experiment. The typical chemical composition of this steel is in Table 6. It is an austenitic stainless steel, with the austenitic phase being stabilized by nickel. It was shown that 316L stainless steel produces corrosion products above certain non-lethal concentrations in its medical applications. This necessitates the use of surface modification of 316L stainless steel, so as to minimize its corrosion and arrest the release of metallic ions and corrosion products. In particular, ceramic coatings play a critical role in providing excellent biocompatibility as well as wear resistance.

The substrates for splat deposition were prepared by cutting a 316L stainless steel sheet of 2 mm in thickness into small pieces of square shapes with dimensions of $(20 \times 20) \text{ mm}^2$. The steel sheet has been already pre-polished before cutting, but during the cutting process some scratches appeared on its surface. The square samples were

grinded by fine sand paper (800, 1000 grit) and polished (6 μ m and 1 μ m diamond paste) with water and ethanol flushing in between the steps, and thereafter, ultrasonically washed in ethanol. Splats were deposited on substrates at room temperature. Roughness of polished specimen surfaces was measured by the roughness tester Surftest SV600, Mitutoyo. The whole measurement was repeated five times. Average values of $R_a = 0.019 \mu\text{m}$ and $R_q = 0.0225 \mu\text{m}$ were calculated.

Table 6: Typical chemical composition of AISI 316L stainless steel [145].

Element	Fe	C	Mn	Si	P	S	Cr	Ni	Mo
Composition (wt.%)	Bal.	0.03	2.0	1.0	0.045	0.03	16.0-18.0	10.0-14.0	2.0-3.0

The dimensions of substrates for coating deposition followed requirements of the laser flash apparatus. They were of cylindrical shapes, 2 mm in thickness and diameter of 12.7 mm. The surface of these substrates was grit-blasted prior to spraying to clean the surface and increase an effective area for mechanical inter-locking between the coating and substrate, thus, improving adhesion of the coating to the substrate.

3.4 Cross-section preparation and observation

The metallographic preparation of samples followed basically the same way with differences determined by particular needs. First step was mounting the samples in two-component (resin + hardener) hardenable compound. Powders were mixed with Gatan epoxy (Model 601.07230 G-1 Epoxy with hardener, Gatan), which has proven the low amount of powder peeling, and hardened in oven at 120 °C for more than 2 minutes. After curing, the samples containing fine powders were manually grinded using SiC sand

papers (P 800 and 1000), followed by diamond slurry polishing using the particle size of 3 μm . Samples were repeatedly rinsed in water and ethanol and ultrasonically washed during the preparation. Powder cross-sections were observed using scanning electron microscope (SEM, JEOL-JSM 5600LV)

Coating samples were mounted into cylindrical solids using Epofix kit (resin M1201025 and hardener M1201026, Struers) and allowed to undergo proper curing. Samples were then grinded with the sequence of SiC sand papers (P 180, 400, 800, 1000 and 2400), followed by a diamond slurry polishing using the particle size of 3 μm , combined with the decreasing pressure and long processing times. Water and ethanol rinsing was also employed as well as ultrasonic washing.

Cross-sectional samples of zirconia and alumina plasma sprayed coatings were observed by optical microscope (Axioskop 2 MAT, Zeiss) equipped with objective lenses of 5x, 10x, 20x, 50x and 100x magnification. Optical micrographs were captured by a digital camera attached to the optical microscope. Initially, semi-transparency and light scatter on the surface of the polished coatings resulted in a low contrast and unfocused pictures. In order to achieve high-quality images of the translucent ceramic coatings, the samples were coated with a gold layer in a coater used for the SEM sample preparation.

3.5 Plasma spray system

For plasma spray implementation, Praxair Surface Technologies, Inc. system (model 4600, Appleton, USA), equipped with the SG-100 plasma spray torch with

3. Materials and experimental setup

tungsten cathode and copper anode was used. The sectional view of the water-cooled spray torch with a radial powder feeding is in Fig. 3.5. Argon was used as a main and a carrier gas during spray. As an auxiliary gas, helium was used. The plasma-forming gas was fed in a vortex into the plasma torch. The diameter of the exit nozzle was 8 mm. The torch was connected to a hydraulic robotic arm (ABB Robotics Products, type IRB2400 M96, Sweden) with six degrees of freedom that enables to adjust a random position of the torch in the robot motion range.

Fig. 3.5: Sectional view of SG-100 plasma spray torch with a radial powder feeding [146].

In order to study the influence of input spray parameters such as net energy; main, auxiliary and carrier gas flow rates; powder feed rate and spray distance on the powder particle in-flight characteristics, the spray torch was attached to a holder mounted in the cubical frame. This frame enables orthogonal adjustment in respect to the components of the SprayWatch monitor system. Spray parameters were changed according to the particular experimental design and will be specified for each experimental approach. Based on the results of these experiments, sets of spray parameters for the splat and coating depositions were compiled. Sometimes, these parameters were modified; e.g.,

during the coating depositions the spray distance was kept the same for all the samples. Basic sets of spray parameters used throughout the major part of the experiments are listed in Table 7.

Table 7: Compiled sets of plasma spray parameters.

Set number	Net energy (kW)	Main gas Ar .10 ⁻⁴ (kg/s)	Auxiliary gas He .10 ⁻⁴ (kg/s)	Carrier gas Ar .10 ⁻⁴ (kg/s)	Powder feed rate (g/min)	Spray distance (mm)
1	6	8.4	0.4	0.7	2	50
2	10	12.6	0.8	2.1	2	100
3	14	12.6	0.8	1.4	2	100

During a splat deposition, powder particles were first sprayed into the air to enable measurement of their in-flight characteristics by the SprayWatch system (Fig. 3.6). Once sufficient data had been gathered, the spray gun was moved upwards, where stainless steel substrates were mounted in a special holder at accurately the same spray distance as used for the data collection (Fig. 3.7). In this holder, substrates were shielded by a perforated plate with mesh of holes of 1 mm in diameter and separated by 1 mm walls that reduced the number of particles impacting the substrate surface. Every time, two samples were mounted above each other in the way of passing spray torch, to provide enough splats for later analysis. Splats were deposited by means of only one pass of the spray gun over the substrate surface. The amount of deposited particles and position of the plasma jet with respect to the substrates were controlled on the glass slides attached to the sample holder.

3.6 SprayWatch monitor system

SprayWatch (Oseir Ltd., Tampere, Finland) is an imaging system for diagnostics

3. Materials and experimental setup

Fig. 3.6: SprayWatch camera to the plasma spray jet and the sample holder adjustment.

Fig. 3.7: Schematic of the holder used for a single splat deposition.

3. Materials and experimental setup

and monitoring of various thermal spray processes. It is based on a fast shutter digital CCD camera, digital image processing and special spectrally resolving optics. The optics, together with the computer control of the camera and a dedicated image processing software enables on-line measurement of velocity, temperature, flux, heading and the position of in-flight particles within an extended volume in the spray jet, together with the parameters of the spray plume such as brightness, width and angle. Fig. 3.8 shows the SprayWatch thermal spray monitor schematically. The main specifications and capabilities of the thermal spray monitor are given in Table 8. The measurement volume is adjustable from $(18 \times 14 \times 5) \text{ mm}^3$ to $(36 \times 28 \times 30) \text{ mm}^3$ [147], [148].

Fig. 3.8: SprayWatch thermal spray monitor consists of a camera unit with spectrally resolving optics and an industrial PC [147].

SprayWatch uses a high-quality, fast shutter CCD camera to create digital images of the spray. It means that instead of just one or two photodetectors looking at a point-like measurement volume, there is an array of hundreds of thousands of small

photodetectors covering the measurement volume. Digital images taken with a short exposure time to stop the high-speed particles are processed on a dedicated control computer to give the measurement data. The algorithm identifies individual particles in the images and measures their characteristics.

Table 8: Main specifications of SprayWatch measuring system [148].

Measured parameter	Range	Accuracy
Particle velocity (m/s)	1 – 2000	0.1 – 5
Particle temperature (°C)	~ 1000 – 4000	1
Relative particle flux (detected particles/s)	10 – 500	-
Spray position (mm)	-12 - +12	0.01
Spray angle (deg)	-10 - +10	0.25

Particle velocity is measured by a time-of-flight method. The length of the particle traces on the CCD detector is measured by the image processing algorithm and is then converted to velocity by dividing by the known camera shutter time.

Particle temperature can be measured with two different methods. A special dichroic double mirror can be used to measure temperatures of individual in-flight particles above approximately 2000 °C (particle surface temperature). The CCD chip of the SprayWatch camera system is partly covered by two optical filter stripes. This filter combination allows measurement of the radiation intensity of the particle flow in the two wavelength ranges. Temperature of the particle flow can thus be calculated using two-colour pyrometry.

When using the filter stripes Fig. 3.9, radiation illuminated by the in-flight particles is integrated during (5 – 100) ms time. The detected intensity does not come from any single particle, but from all particles that have passed the measurement volume during the integration time. Thus, the measured two-colour temperature is the effective spray

temperature that is related to the average particle temperature but weighted towards hotter particles. It can be shown that the effective spray temperature is theoretically about 40 – 100 degrees higher than the average two-colour particle temperature. In the plasma spray the spectral radiation of plasma compounds or an evaporated spray material may cause significant errors when the temperature of the spray is below 1800 °C or when the measurement is done near the torch nozzle.

Fig. 3.9: Measurement principle of the average particle temperature in the SprayWatch system [147].

The SprayWatch system does not normally use additional light sources to detect the particles, but relies purely on the spontaneous light emitted by the hot sprayed particles themselves. To detect cold particles, HiWatch, a diode laser system, can be used to illuminate the measurement volume of the SprayWatch monitor system. This system enables, in addition to the visualization of the process, the measurement of several flow and spray parameters such as velocity, size and shape of particles, droplets or bubbles, spray pattern etc.

3.7 Laser flash method

The laser flash method is an experimental technique used to measure thermal diffusivity of materials. In our experiments the LFA 427 apparatus (Netzsch, Germany) was used. The flash method is based upon the measurement of the temperature rise on the back face of a thin disk-shaped sample caused by a short energy pulse on the front surface. The sample is placed in a vacuum furnace and isothermally heated at a uniform temperature. Then, a short pulse from an unfocused laser irradiates one side of the sample. The temperature rise on the opposite sample face is measured by an infrared detector. The temperature distribution inside the test piece depends on the thermal diffusivity of the material. A high-speed recorder collects data representing the temperature rise – thermogram (Fig. 3.10). The thermal diffusivity is calculated from the time required to reach one-half of the peak temperature in the temperature-time curve ($t_{0.5}$) and the thickness of the sample (L). In this experiment a solution proposed originally by Parker was used following relation

$$\alpha = 0.138785 \frac{L^2}{t_{0.5}} \quad (11)$$

The thermal conductivity can be then determined using the following formula:

$$k = \alpha C_p \rho \quad (12)$$

where k is the thermal conductivity, α is the thermal diffusivity, C_p is the specific heat, and ρ is the density of the sample material [149], [150], [151], [152], [153].

Fig. 3.10: Temperature rise with time.

Regular thermal diffusivity measurement requires the specimen to be opaque to both wavelengths of the laser pulse and the infrared detector. The basic assumptions for the measurement are that all the laser energy is absorbed at the front surface and the IR detector only measures thermal radiation of the rear surface. The thermal barrier coating materials are typically translucent; therefore, the conventional treatment is to put opaque coatings on both sides of the sample (graphite or metallic films such as Au or Au/Pd). The Au or Au/Pd coatings are only good up to about 900 °C; however, typical TBC application requires data up to 1400 °C. The high-temperature measurement requires some special sample preparation such as thick graphite coating (four to five passes) or Pt coatings.

It was shown that measured values of thermal diffusivity differ for the TBCs with and without opaque coatings. The thermal diffusivity values obtained from measurements

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3. Materials and experimental setup

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of samples with opaque coatings, or of thickness greater than the infinite thickness (the thickness of the material beyond which semi-transparency can be neglected), determine, that the heat transfer through the TBC coating is only via the phonon mechanism. Otherwise, contribution of the photon mechanism must be taken into account due to the absorption and reflection of the incident radiation. The influence of the darkening the sample surfaces in laser flash measurements has been studied. It was shown that the darkening by painting affects the results in less significant way as compared to spraying of such darkening layers. The relative error induced by painting was estimated to be less than 2 %. Also the influence of the sample surface grinding was shown to have an effect on measured values of thermal diffusivity [154], [155], [157], [158], [159], [160].

Even with opaque coatings, TBCs have other characteristics that make the diffusivity measurements difficult. Free-standing coatings are frequently used for the thermal diffusivity measurement. Air plasma sprayed TBCs have the typical thickness of 300 μm or less and have very low thermal conductivities. Under these conditions, the front and rear sample surface temperatures will increase much more after the laser pulse as opposed to a thicker sample with moderate thermal conductivity. The excessive temperature increase could drive the IR detector into a nonlinear temperature-voltage response and thereby cause significant errors in the measured diffusivity values. Laser power levels should be large enough to obtain a good signal-to-noise ratio, yet not result in the excessive rear surface temperature rise (i.e. $\Delta T > 5\text{ }^{\circ}\text{C}$). Significant error will also occur if the thermal diffusivity measurements are carried out too soon after firing a warm

detector with nitrogen because the IR detector has not reached equilibrium. Next, a possible error can arise if the laser pulse duration is long in comparison to the heat transport time that is needed to reach half of the maximum temperature change at the back of the test specimen [154], [156]. Necessary adjustments, in terms of laser pulse characteristics, of the measuring apparatus were done prior the measurement in order to obtain good signal-to-noise ratio. Accuracy of the LFA 427 apparatus as given by Netzsch is about 5 %.

3.8 Electrochemical impedance spectroscopy

The electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell. Impedance Z is a measure of the ability of a circuit to resist the flow of electrical current. The impedance can be represented as a complex number composed of a real and an imaginary part. In the Nyquist plot, the real part is plotted on the x -axis and the imaginary part on the y -axis of a chart (Fig. 3.11). In this plot, the y -axis is negative and each point on the Nyquist plot is the impedance at one frequency; low frequency data are on the right side of the plot and higher frequencies are on the left. The semicircle is characteristic of a single “time constant”. The electrochemical impedance plots often contain several semicircles, usually only a portion of semicircle is seen. Another popular representation method is the Bode plot. The impedance is plotted with a log frequency on the x -axis and both the absolute values of the impedance and the phase-shift between the potential and current on the y -axis (Fig. 3.12).

Fig. 3.11: Nyquist plot with impedance vector.

The system must be at a steady state throughout an EIS spectrum measurement, otherwise the data analysis tools give inaccurate results. In practice, a steady state can be difficult to achieve. The cell can change through adsorption of solution impurities, growth of an oxide layer, build up of reaction products in solution, coating degradation, temperature changes, etc. EIS data are generally analysed in terms of an equivalent circuit model – model whose impedance matches the measured data. The type of electrical components (resistor, capacitor, inductor) in the model and their interconnections (in parallel or in series) control the shape of the model impedance spectrum. The model parameters (e.g. the resistance value of a resistor) control the size of each feature in the spectrum. Both these factors affect the degree to which the model impedance spectrum matches a measured EIS spectrum. Each of the model components postulated should come from knowledge of the physical processes in the electrochemical cell (physical model). Fitting the model parameters that cause the best agreement between a model impedance spectrum and a measured spectrum is computerized using a non-linear least square fitting algorithm (NLLS).

Fig. 3.12: Bode plot with one time constant.

EIS has been used in assessing the quality and performance of plasma sprayed coatings in applications such as sensing materials, corrosion protective coatings for automotive components and also thermal barrier coatings [231], [232], [233], [234], [235], [236], [237], [238]. It was shown that the validity of using EIS to evaluate the thermal conductivity of free-standing TBCs is based on the fact that EIS is sensitive to the change in microstructure and pore evolution of the TBC. Electrical conduction in EIS depends on the conductivity of the electrolyte and micro-structural features of the free-standing TBCs, including porosity, contact at the interfaces and damage through which electrolyte can penetrate.

In this experiment, EIS was carried out in a three-electrode system, which compensates for the solution resistance between the counter and reference electrodes. Autolab PG30 (Eco Chemie B.V. Utrecht, The Netherlands) frequency response analyser and software were used for the data acquisition and model fitting. The electrolyte

3. Materials and experimental setup

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employed in measurement was 0.01 M potassium Ferri/Ferro Cyanide $K_3Fe(CN)_6/K_4Fe(CN)_6 \cdot 3H_2O$. A platinum electrode was used as a counter electrode; a standard calomel electrode was used as a reference electrode. About 10 minutes was allowed for the electrolyte penetration through open pores within TBCs and for the system to achieve a steady state during each measurement. AC potential amplitudes of 5 mV for alumina and 20 mV for zirconia coatings were applied over the frequency range of $(10^{-2} - 10^6)$ Hz. Three measurement iterations were carried out for each specimen.

4. INFLUENCE OF SPRAY PARAMETERS ON PARTICLE VELOCITY AND TEMPERATURE

The plasma spray is a coating deposition process influenced by a large number of parameters and comprising of a variety of complex interactions, such as plasma jet - powder particle, powder particle - substrate surface etc. These interactions can often give rise to some limitations in the plasma spray process, especially in terms of process repeatability, when aiming for desired properties of final coatings. A great deal of research is currently devoted to understand how varying spray parameters affect the in-flight particle velocity and temperature. The particle velocity and temperature have strong influence on the splat formation and morphology and thus building up of a coating and its final properties (porosity, residual stresses, thermal properties, etc.) [147], [164], [165], [166]. That is why the knowledge of plasma spray parameters' influences and diagnostics on in-flight particles are very important for better understanding of the plasma spray process. In spite of the fact that some attempts in a closed loop control of the plasma deposition process have been done [164], the plasma spray is still a process based on a trial and error, where spray parameters are chosen, coatings are prepared and after that their properties are investigated.

In order to improve the understanding of how final coating properties in the plasma spray process can be influenced by input parameters, through the impacting particle velocity and temperature, an experiment studying effects of six plasma spray process parameters has been conducted. The six parameters were net energy; main, auxiliary and

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4. Influence of spray parameters on particle velocity and temperature

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carrier gas flow rates; powder feed rate and spray distance. In the present experiment, YSZ powder particles with the size range of $(45 - 75) \mu\text{m}$ were plasma sprayed into the air. Their in-flight characteristics were measured by the SprayWatch monitor system equipped with a fast shutter CCD camera located at the right angle to the plasma jet axis. The distance between the jet axis and the camera was 250 mm. Measurement of the particle velocity and temperature was delayed every time, until the steady state of the plasma spray process had been achieved. The experimental data were then gathered for at least one minute and saved by the controlling computer. After that, the spray process was stopped, input parameters re-set and the whole measurement procedure was repeated with the new set of spray parameters.

The level of carrier gas flow rate can significantly influence penetration, and thus, the subsequent position of particles in the plasma jet. The particle position in the plasma jet influences heat and momentum transfer from the plasma jet, and thus, its velocity and temperature. To partially avoid this problem, when a fixed value of the carrier gas flow rate was used in the experiments, the spray gun was adjusted so that the direction of a powder injection into the plasma jet was in plane defined by the plasma jet axis and the SprayWatch camera detecting axis. This will not help to obtain the optimal particle velocities and temperatures; particles still can be in a peripheral region of the plasma jet due to the different velocities of the plasma jet at the point of the powder injection. However, this ensures the detection of such particles, in case they are located in a SprayWatch camera detection volume, and provides the same measurement conditions for all the measurements done.

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4. Influence of spray parameters on particle velocity and temperature

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It is necessary to note, that the velocity and temperature data records obtained from the SprayWatch software are average values gathered over the short period of time. Thus, mere observations of the mean values can be misleading and careful interpretations of the measured distributions are necessary. For example, the hotter plasma jet heats up larger and colder particles which have not been detected by the system previously. These larger, additionally detected particles can lower the average of the temperature distribution. Another example can be the usage of a non-optimal powder feed rate value. There are then faster particles with high temperatures in the center of the plasma jet and slow, colder ones in the periphery of the plasma jet. Providing that all of them are detected, an average value of velocity or temperature does not give a precise image about the real sprayed particle characteristics. Also phenomenon called “saltation”, i.e. accumulation of powder particles in the powder feeding hose or at the injector exit to the plasma torch and sudden powder release can influence plasma jet properties and cause fluctuations in the resulting particle velocities and temperatures. Such behaviour is as well closely related to the values of plasma and carrier gas flow rates. In-flight velocity and temperature attained by powder particles can be also influenced by arc fluctuations. Problems with powder saltation were experienced when using low values of parameters such as net energy, main and auxiliary gas flow rates in this experiment.

All these phenomena, influencing the in-flight particle velocity and temperature, need not necessarily be found in a particular time dependence of the characteristic average value. Averaging can mask some of the phenomena. Therefore, it is important to deal also with the recorded data standard deviation, where these irregularities can be

4. Influence of spray parameters on particle velocity and temperature

sometimes revealed. Example of an average temperature record, showing standard deviation for individual measurements, affected by unsteady powder feeding, is shown in Fig. 4.1. Such data were not considered as representative of system settings; the measurements were usually repeated or performed for prolonged time with respective data after-treatment.

Fig. 4.1: Example of an average temperature record, with the standard deviation for individual measurements, influenced by unsteady powder feeding.

Two experimental approaches were used to investigate the influence of input spray parameters on the particle in-flight temperature and velocity; i.e., (i) the “several parameters, one at a time” method, and (ii) the Taguchi design of experiments method.

4.1 “Several parameters, one at a time” method

Generally, the most common test plan is to evaluate the effect of one parameter on the observed process characteristic. The “several parameters, one at a time” method evaluates the effect of one parameter, which is changed one level at a time, while keeping

4. Influence of spray parameters on particle velocity and temperature

the rest of the parameters constant. The main limitation of this method is that no interactions among parameters studied can be observed. Concept of such an experiment dealing with the influence of input plasma spray parameters, namely net energy; main, auxiliary and carrier gas flow rates; powder feed rate and spray distance, can be seen from Table 9. There are fixed values of all parameters, together with the range over which each particular parameter influence has been observed and the step change for each parameter.

Table 9: Fixed set of spray parameters and parameter variation ranges.

Spray parameter	Fixed value	Step	Variation range
Net energy (kW)	14	1	10 – 16
Main gas flow rate, Ar ($\times 10^{-4}$ kg/s)	11.22	0.70	8.42 – 11.22
Auxiliary gas flow rate, He ($\times 10^{-4}$ kg/s)	0.56	0.07	0.42 – 0.84
Carrier gas flow rate, Ar ($\times 10^{-4}$ kg/s)	1.68	0.28	0.56 – 2.80
Powder feed rate (g/min)	8	2	4 – 16
Spray distance (mm)	120	10, 20	100 – 250

In order to obtain reliable results, data of the particle velocity and temperature were gathered for at least 60 seconds for each set of parameters. The time development of the particle velocity and temperature is shown for the case when net energy was changed over the range from 10 to 16 kW with step of 1 kW (Fig. 4.2 and Fig. 4.3). Each point in diagram represents the average value of proper characteristic (velocity or temperature) calculated by the SprayWatch software after data collection over some period of time. The standard deviation for each of these points is also determined. However, this is not included in the diagrams, because those would be then overfilled and it would be difficult to observe any trend in the data average values. From the figures with the time dependance, it is obvious that with increasing net energy, both the velocity and temperature of flying particles increased significantly.

4. Influence of spray parameters on particle velocity and temperature

Fig. 4.2: Change of the particle velocity time dependance with net energy.

Fig. 4.3: Change of the particle temperature time dependance with net energy.

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4. Influence of spray parameters on particle velocity and temperature

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Since these diagrams might not provide an easy survey, especially when more of the parameter values were used, i.e., more curves in the diagram, the diagrams with average values will be used in the following. In Fig. 4.4 there are average values of the powder particle velocities and temperatures plotted as functions of various spray parameters changed over the particular parameter range of values. Vertical bars in diagrams represent standard deviations calculated for each measurement characterized by specific parameter settings. Average relative error for the velocity measurements was estimated to be about 2.3 %, for the temperature measurements this value is close to 1%. The biggest errors for both, particle velocity and temperature, come from the measurements at the end of the spray distance value range. These can be related to existence of sparser plasma jet and particle flow at this distance from the nozzle exit, which can influence measurements. Actual values of the average particle velocity and temperature for all the parameter combinations can be found in Table 10.

It is obvious that with the increasing *net energy*, both the particle in-flight velocity and temperature increased. For the particle velocity the increase from 128 m/s to 162 m/s is very significant and corresponds to almost 27 % increase. Increase in net energy resulted in the particle temperature increase from 2343 °C to 2467 °C, which is rather moderate being less than 6 %. Generally, an opposite trend in the temperature development would be expected. With increasing net energy, the increase in particle velocity corresponds to the shorter particle's residence time in the plasma jet, and thus, the shorter time for the possible heat transfer from the plasma jet to the particle. Nevertheless, the effect of shorter residence time is compensated by plasma temperature

4. Influence of spray parameters on particle velocity and temperature

Fig. 4.4: Dependence of the average particle velocity and temperature on a step change of various parameters, such as net energy; main, auxiliary and carrier gas flow rates, powder feed rate and spray distance. Vertical bars represent standard deviations.

4. Influence of spray parameters on particle velocity and temperature

Table 10: Average particle velocity and temperature evolution with a step change in input spray parameters.

Net energy (kW)	10	11	12	13	14	15	16				
Velocity (m/s)	128	136	143	149	154	158	162				
Temperature (°C)	2343	2398	2397	2422	2431	2434	2467				
Main gas (x10 ⁻⁴ kg/s)	8.42	9.12	9.82	10.52	11.22						
Velocity (m/s)	147	145	150	157	152						
Temperature (°C)	2486	2452	2464	2456	2434						
Auxiliary gas (x10 ⁻⁴ kg/s)	0.42	0.49	0.56	0.63	0.70	0.77	0.84				
Velocity (m/s)	146	149	156	157	160	161	166				
Temperature (°C)	2431	2431	2437	2436	2440	2443	2449				
Carrier gas (x10 ⁻⁴ kg/s)	0.56	0.84	1.12	1.40	1.68	1.96	2.24	2.52	2.80		
Velocity (m/s)	142	150	154	153	147	141	136	123	125		
Temperature (°C)	2371	2437	2494	2497	2477	2440	2429	2389	2278		
Powder feeding (g/min)	2	4	6	8	10	12	14	16			
Velocity (m/s)	146	144	148	144	145	143	144	128			
Temperature (°C)	2468	2463	2478	2463	2479	2456	2473	2414			
Spray distance (mm)	100	110	120	130	140	150	170	190	210	230	250
Velocity (m/s)	164	163	158	157	149	148	138	131	123	122	113
Temperature (°C)	2558	2508	2455	2432	2421	2418	2402	2337	2320	2312	2288

increase due to the increase in the net energy. However, it was shown that with increase in net energy most of that energy is utilized for ionization (or dissociation) of plasma gas and also the higher heat loss to the walls of the plasma torch and electrodes was reported [167], [169], [170]. Therefore, the increase in particle temperature is not so big as it was indicated by results obtained above.

As the second parameter observed, *main gas (Ar) flow rate* was changed over the range of (8.42 to 11.22)x10⁻⁴ kg/s with a step of 0.70x10⁻⁴ kg/s. No explicit influence

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4. Influence of spray parameters on particle velocity and temperature

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or trend in experimental data was observed with the change of the main gas flow rate. Argon ions are quite heavy and thus can transfer momentum to particles very well [174]. Therefore, increasing the argon flow rate should influence the powder particle velocity. Increase in the argon flow rate is related to the melting behaviour of the powder through the well known relation of the particle velocity and the particle dwelling time in the plasma jet during spraying. However, no such phenomena were observed during this experiment.

In contrast to the main gas flow rate, a change in the helium *auxiliary gas flow rate* over the range of $(0.42 - 0.84) \times 10^{-4}$ kg/s raised the average particle velocity. Helium is added to the plasma gas mixture to enhance the heat transfer toward the powder particles. Increase in helium flow rate probably lead to heating of faster particles that resulted in increase of the particle velocity over the explored range by almost 14%, while average temperature remained unchanged. In current experiment the addition of at most 7 wt.% of helium into gas mixture was not sufficient to affect the particle temperature.

The dwell time of particles in the plasma plume influences not only the heat flux from plasma to the particles, but also the internal heat flux of the particles, which is also affected by the thermophysical properties and morphology of the sprayed powder and composition of plasma gas. Throughout this experiment the Biot number varied between 0.67 and 0.69, which suggests similar conditions for particle heating [171]. This indicates that the heat conduction inside the particles is slower than on its surface and that the temperature gradients inside the powder particles are non-negligible. No influences of changing argon flow rate on particle velocity and helium flow rate on particle

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4. Influence of spray parameters on particle velocity and temperature

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temperature are probably caused by narrow range of parameter values. Some indications of such effects, when using wider range of values, can be found in Table 11 where more critical main and auxiliary gas flow rates resulted in significant changes in particle in-flight velocity and temperature as predicted above.

As for the *carrier gas flow rate*, the results suggest the existence of an optimal value for this parameter at about 1.2×10^{-4} kg/s, at which the particle velocity and temperature reached maximum. This effect is explained by a different depth of penetration of the particles into the plasma jet combined with deflection of the plasma jet due to the carrier gas flow rate. Under an optimal value of the carrier gas flow, particles penetrate into and remain in the central portion of the plasma jet. With insufficient powder injection velocity or for high injection velocities, when overshooting of the central part of the plasma jet occurs, particles remain at peripheral, slow regions of the plasma jet [175], [176]. Note that the peak of the optimal carrier gas flow rate is not constant. Its position can be shifted once any of the spray parameters is changed, especially those influencing fairly the velocity of the plasma jet. Another important fact is related to the particle detection within the measurement volume of the SprayWatch camera. Assuming different depth of powder particles penetration into the plasma jet and thus their different position in the plasma jet, the different part of the plasma jet with powder particles falls in the middle of the SprayWatch measurement volume for different value of the carrier gas flow rate.

As the data show when increasing the carrier gas flow rate from low values, at which the plasma jet remains unaffected, the particle temperature and velocity increased

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4. Influence of spray parameters on particle velocity and temperature

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due to the better penetration of the particles into the plasma jet. Above the value of 1.2×10^{-4} kg/s, which corresponds to 10 % of the total plasma gas flow rate - the critical value for the plasma jet deflection, the particle velocity and temperature decreased. The rate of decrease for particle temperature is lower than the previous increase that could be due to the reduced effect of excessive penetration by the plasma jet deflection. The values obtained for carrier gas flow rate of 2.8×10^{-4} kg/s are probably influenced by a too high carrier gas flow rate corresponding to almost 24 % of the plasma gas flow rate (gases mixing, detection of the plasma jet periphery), as indicated by higher standard deviations.

Possible effect of the changing *powder feed rate* dwells in the fact that the same heat and momentum of the plasma jet have to be transferred to the different amount of sprayed powder. The powder feed rate that corresponds approximately to 30 % of the plasma gas mass flow is considered to be a critical value. It is obvious then that with the higher powder feed rate, the particle velocity and temperature should decrease. No such trend was observed in the presented results when the powder feed rate was changed from 2 to 16 g/min ($\sim 3 - 22$ % of the plasma gas mass flow). Decrease of particle velocity and temperature for the highest value of the powder feed rate of 16 g/min might give some indication about beginning of described phenomenon, when the powder feed rate reached 22 % of the plasma gas mass flow.

As the last parameter the *spray distance* was taken into account. Strong influence of the spray distance on the particle velocity and temperature is evident from Fig. 4.4. With decrease in the spray distance from 250 to 100 mm, both the particle velocity and

4. Influence of spray parameters on particle velocity and temperature

temperature increased significantly by almost 45 % and almost 12 %, respectively. Such behavior was expected since after injection the powder particles at the room temperature are rapidly heated and accelerated. In this region the particle velocity and temperature would increase with the increasing spray distance. This region of the plasma jet was not investigated in this experiment because of the detection limit of the SprayWatch monitor system. Particles during their flight exit the plasma jet, the subsequent deficiency of a heat and a momentum transfer start to slow and cool them down at the end of the plasma plume, as well as later on in the surrounding cold air. Measurements at large spray distances were probably influenced by sparser nature of the plasma plume and particle flow as indicated by increase in standard deviations.

Temperature	High	LH	HH
	Low	LL	HL
		Low	High
		Velocity	

Fig. 4.5: Critical combinations of the particle velocity and temperature.

Based on a trial and error principle, the results presented above were used to compile more than 40 different combinations of spraying parameters. Their influence on the particle velocity and temperature was tested. Greater variety in the parameter values was used for all of six parameters. From the data obtained by SprayWatch, the average

4. Influence of spray parameters on particle velocity and temperature

velocity and temperature were calculated for each set of parameters. Results were plotted in a temperature versus velocity diagram. The very first idea about the experiment design was to prepare splats from particles deposited under four different critical conditions (Fig. 4.5).

Table 11: Ten sets of spray parameters used for YSZ splats preparation.

Set number	Net energy (kW)	Main gas Ar (*)	Auxiliary gas He (*)	Carrier gas Ar (*)	Powder feed rate (g/min)	Spray distance (mm)	Average velocity (m/s)	Average temperature (deg C)
1	2	1.40	0.14	1.40	2	50	19	2720
2	2	1.40	0.14	8.42	2	50	19	2840
3	3	5.61	0.14	1.40	6	50	77	3356
4	6	8.42	0.56	1.68	2	75	102	2875
5	8	11.22	0.56	1.68	8	200	106	2344
6	12	11.22	0.42	1.68	8	200	111	2378
7	3	5.61	0.28	1.68	2	75	32	2537
8	3	4.21	0.84	1.68	2	50	61	3275
9	14	8.42	0.84	1.40	2	80	144	3207
10	14	11.22	0.84	1.40	2	80	162	2931

(*) = $\times 10^{-4}$ kg/s

According to this criterion, ten sets of the spray parameters were chosen (Table 11). Preferences were given to those sets of parameters whose “resulting points” in the temperature vs. velocity diagram were located in the proximity to one of the four corners of the diagram. These sets were later used for deposition of the YSZ powder of particle size range of $(45 - 75) \mu\text{m}$ onto the polished stainless steel substrates. Unfortunately, the powder particle velocity and temperature, influenced mainly by the net energy, spray distance and He flow rate, were highly correlated which made it impossible to find proper spray conditions (sets of parameters) to achieve the *HL* and *LH* combinations of in-flight particle characteristics in Fig. 4.5. Moreover, the extremely low values of parameters such as net energy, main and auxiliary gas flow rates caused

4. Influence of spray parameters on particle velocity and temperature

the arc/plasma jet instabilities that were indicated by visible large fluctuations of the arc length and size. This resulted in differences in repeatedly measured particle velocities and temperatures, disabling the repeatability of the spray conditions. Thus, the presumed “square” with deposition points in the temperature vs. velocity diagram corners, or their proximity, has not been achieved (Fig. 4.6).

Fig. 4.6: Temperature versus velocity of in-flight particles sprayed under conditions listed in Table 11.

A different criterion was therefore implemented to select the samples for further analysis. YSZ splats deposited at the approximately same temperature but with different velocities were chosen for analysis that can be found elsewhere [177]. Corresponding points in the temperature vs. velocity diagram are highlighted in Fig. 4.6 as are the respective sets of spray parameters in Table 11.

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4. Influence of spray parameters on particle velocity and temperature

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In order to support or disprove described results, and to implement sophisticated statistical approach to the problem, the Taguchi design of experiment was introduced.

4.2 Taguchi design of experiment

The Taguchi design of experiment is based on the implementation of a particular number of runs during which several parameters are varied, at different combinations of parameter levels, according to orthogonal arrays [179], [180], [181]. The orthogonality here means that the parameters can be evaluated independently; i.e., the effect of one parameter does not interfere with the estimation of the effect of another one. Analysis of variance (ANOVA) was used for the statistical evaluation of measured data from the Taguchi design of experiment. ANOVA is a mathematical decision tool based on the comparison of the data variation due to the parameter change with the overall variation of experimental data. How to perform the ANOVA analysis can be found elsewhere [179]. Statistically, there is a tool which provides a decision at some confidence level as to whether these variation estimates are significantly different. It is an F test, which is simply a ratio of sample variances. The F ratio serves only to decide whether a particular parameter has a statistically significant effect on the observed characteristic (particle velocity or temperature) at some level of confidence; it does not say anything about the size of the effect.

Confidence ($1-\alpha$), usually introduced as a percentage value, means that there is some chance of a mistake in results interpretation. A high confidence may result to situation where a selected parameter, in spite of having the effect on observed

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4. Influence of spray parameters on particle velocity and temperature

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characteristic, is rejected. On the other hand, when the confidence level is excessively low, effect of the selected parameter can be taken into account even when, in fact, this parameter does not influence the observed characteristic.

To determine whether the F ratio of two sample variances is statistically large enough, three pieces of information are considered (the confidence level necessary, the degrees of freedom associated with the sample variance in the numerator and in the denominator). Calculated value of the F ratio is then compared with so called criterion (the F ratio from the tables). If the calculated value of the F ratio is greater than the tabulated value, this means that with at least say 90% confidence, the two estimates of variance are believed to be unequal. The parameters which have the F ratio larger than the criterion are believed to influence the average value for the population of observed characteristic, and parameters which have the F ratio less than the criterion are believed to have no effect on the average.

A simple repetition method was performed for the trial selection. The simple repetition means that any trial has an equal opportunity of being selected for the first test, but once that trial is selected, all the repetitions are tested for that trial. Another possible method is a complete randomization (drawing numbers from a hat) for trials as well as for repetitions. The different methods of the randomization affect error variance in different ways. The complete randomization allows the longer time to transpire between repetitions in a given trial. Because of this, unknown and uncontrolled factors that may be varying during an experiment may make the repetition-to-repetition variation larger for the complete randomization process. Similarly simple repetition, because of

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4. Influence of spray parameters on particle velocity and temperature

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the generally longer times transpiring between trials, will show larger trial-to-trial variation as compared to the complete randomization. The increased trial-to-trial variation with the decreased repetition variation may or may not tend to make factors appear significant in ANOVA, when in fact they are not.

In the present Taguchi design of experiment three levels for value of each parameter were selected and combined. The experimental design with results of measured average particle velocities and temperatures is in Table 12. For each set of parameters, two measurements (repetitions) were conducted. Tabulated values of the F test characteristic with 2 and 23 degrees of freedom used in this study are in

Table 13. Complete results of the ANOVA analysis are in Table 14 and Table 15.

From the tables it can be seen that the confidence of 90 % is too low for presumption of the individual parameter effect on the measured particle in-flight characteristics. Also, 95 % confidence does not provide any decisive information. Ostensible importance of all parameters for lower levels of confidence can be caused by using too wide range of a given parameter, which increases variance of the experimental data due to the parameter change. Another possible reason is large variation due to the effect of some parameter (such as net energy in case of velocity and net energy and spray distance parameters in case of temperature) that results in low error variation. Such data yield high calculated F ratios that assign significant influence to parameters that, in fact, do not have any strong effect [179]. Selecting the values for parameter levels is very sensitive. Too narrow range of values of the influential parameter, can lead to small variation due to a change of the parameter value and thus rejection of the parameter

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4. Influence of spray parameters on particle velocity and temperature

Table 12: Taguchi design of experiment with results of average velocity and temperature.

Run	Net energy (kW)	Main gas Ar (*)	Auxiliary gas He (*)	Carrier gas Ar (*)	Powder feed rate (g/min)	Spray distance (mm)	Average velocity (m/s)		Average temperature (deg C)	
							1	2	1	2
1	6	8.42	0.42	0.70	5	100	81	89	2289	2228
2	6	12.62	0.84	1.40	10	150	104	105	2144	2155
3	6	16.83	1.26	2.10	15	200	115	105	2087	2055
4	11	8.42	0.42	1.40	10	200	97	90	2265	2279
5	11	12.62	0.84	2.10	15	100	139	136	2390	2379
6	11	16.83	1.26	0.70	5	150	147	148	2239	2233
7	16	8.42	0.84	0.70	15	150	144	142	2332	2310
8	16	12.62	1.26	1.40	5	200	141	139	2293	2299
9	16	16.83	0.42	2.10	10	100	164	173	2459	2468
10	6	8.42	1.26	2.10	10	150	99	101	2098	2084
11	6	12.62	0.42	0.70	15	200	95	94	2151	2106
12	6	16.83	0.84	1.40	5	100	124	124	2195	2191
13	11	8.42	0.84	2.10	5	200	98	101	2189	2232
14	11	12.62	1.26	0.70	10	100	138	152	2375	2311
15	11	16.83	0.42	1.40	15	150	122	132	2197	2241
16	16	8.42	1.26	1.40	15	100	154	153	2683	2679
17	16	12.62	0.42	2.10	5	150	135	132	2285	2280
18	16	16.83	0.84	0.70	10	200	146	157	2164	2157

(*) = $\times 10^{-4}$ kg/s

Table 13: Tabulated values of *F* test with 2 and 23 degrees of freedom.

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

Table 14: Results of ANOVA analysis for the particle velocity.

Parameter	Sum of squares	Degrees of freedom	Mean of sum of squares	F ratio	Confidence		
					90%	95%	99%
Net energy	12434.62	2	6217.31	202.35	Effect	Effect	Effect
Main gas	3994.43	2	1997.21	65.00	Effect	Effect	Effect
Auxiliary gas	1467.45	2	733.73	23.88	Effect	Effect	Effect
Carrier gas	99.40	2	49.70	1.62			
Feed rate	261.41	2	130.71	4.25	Effect	Effect	
Spray distance	2579.61	2	1289.81	41.98	Effect	Effect	Effect
Error	706.68	23	30.73				
Total	21543.60	35					

4. Influence of spray parameters on particle velocity and temperature

Table 15: Results of ANOVA analysis for the particle temperature.

Parameter	Sum of squares	Degrees of freedom	Mean of sum of squares	F ratio	Confidence		
					90%	95%	99%
Net energy	290596.50	2	145298.25	60.20	Effect	Effect	Effect
Main gas	40047.71	2	20023.86	8.30	Effect	Effect	Effect
Auxiliary gas	15488.40	2	7744.20	3.21	Effect		
Carrier gas	25532.47	2	12766.24	5.29	Effect	Effect	
Feed rate	23705.21	2	11852.61	4.91	Effect	Effect	
Spray distance	275549.10	2	137774.55	57.09	Effect	Effect	Effect
Error	55508.52	23	2413.41				
Total	726427.90	35					

influence on the observed characteristic. On the other hand, a too wide range of values of the uninfluential parameter can result in acceptance of such a parameter effect on the observed characteristic.

Plots of statistically significant parameters can indicate the magnitudes of the effects by the slopes - the higher the slope, the greater the parameter's effect. The *F* ratio in general indicates which parameters should be plotted. Fig. 4.7 and Fig. 4.8 show changes of the average values of the particle velocity and temperature with a change in the level of given parameter. Each point in diagrams represents an average of 12 values of the given characteristic obtained from the measurement at the particular level of parameter; dashed lines represent the overall averages. From the slope of diagrams, one can presume the size of the parameter effect and also its character.

The obtained results are in a good agreement with the results from the first part of the experiment, where influence of one parameter at a time was tested. Apparently, the *net energy* has the strongest influence on both the particle velocity and temperature. Increase in net energy from 6 to 16 kW resulted in more than 44 % and 10 % increase in

4. Influence of spray parameters on particle velocity and temperature

particle velocity and temperature, respectively. Moderate increase in particle temperature with increase in net energy has been explained earlier by consumption of the energy by plasma gas ionization and higher heat losses to the surroundings.

Fig. 4.7: Change of average values of the particle velocity with a change in the level of given parametr.

Fig. 4.8: Change of average values of the particle temperature with a change in the level of given parametr.

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4. Influence of spray parameters on particle velocity and temperature

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Another parameter with strong effect is the *main gas flow rate*. With increase in this parameter the particle velocity increased significantly by 23 %, while particle temperature decreased by less than 4 %. The amount of gas crossing the electric arc in the plasma spray gun determines the properties of the plasma jet such as temperature, velocity, density and size (esp. length), which in turn can influence the in-flight characteristics of introduced powder particles. With increase in main gas flow rate the fixed enthalpy input to the gas is absorbed by increasing amount of gas, and thus, the particle temperature decreased. The *auxiliary gas flow rate* reveals effect on the particle velocity (increase by 13 %). It was indicated earlier, when this parameter was changed separately, by the increase in the average particle velocity. The effect of helium flow rate on the particle temperature was not observed when amount of helium in the plasma gas was changed from 3.5 to 9.7 wt.%. The Biot numbers for used plasma gas compositions were between 0.67 and 0.72, which indicates that the conditions for particle heating were similar throughout the experiment.

The existence of value for the *carrier gas flow rate* at which the maximum particle velocity and temperature are obtained cannot be expected to be revealed by the ANOVA analysis. Inability to reveal this phenomenon dwells in the knowledge of the plasma spray process arrangement. Particles travelling on the periphery of the plasma plume (due to insufficient or too high powder injection velocity combined with the plasma jet deflection) contribute to decrease in the particle in-flight velocity and temperature. Thus, results obtained for low and high values of the carrier gas flow rate do not increase the data variance due to a change in the parameter value. The calculated F ratio is smaller

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4. Influence of spray parameters on particle velocity and temperature

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than the tabulated value, for a given confidence level, and such a parameter is rejected to have any influence on the observed characteristic.

No distinct influence of *powder feed rate* on the particle velocity and temperature was observed. Indeed, the calculated values of ratio of powder feed rate and gas mass flow rate are well below the critical value of 30 % thus no effect due to the powder loading can be expected.

The *spray distance* was recognized to be the second most influential parameter on the particle in-flight velocity and temperature. The increase by more than 19 % and 9 % in the particle velocity and temperature, due to the decrease in spray distance, is in a good agreement with the previously obtained results.

Plotting the experimental data in an actual test order can reveal any strong trends that may have existed during the execution of the experiment. The trends would have to be caused by some unknown, uncontrolled factor(s) that varied during the experiment. In Fig. 4.9 and Fig. 4.10, the diagrams show the relative average velocity and temperature plotted against the actual run order. Both diagrams show an irregular wavy behavior, especially for the higher run orders the sawtooth waveform can be seen. However, the first part (up to the point 8) could raise suspicion about the existence of some uncontrolled factors causing the rise and fall of the measured velocity and temperature.

Since no such factors were expected, based on the knowledge of the spray process, there was a need to find out the probable cause of the measured velocity and temperature behavior. It was revealed that such behavior is in a total agreement with the combined effect of the three most influential plasma spray input parameters. Effects of these

4. Influence of spray parameters on particle velocity and temperature

parameters, namely the net energy, spray distance and main gas flow rate, were summarized in one function and compared with the behavior of the relative average velocity and temperature.

Fig. 4.9: Average velocity and its parameter function in respect to a run order.

Fig. 4.10: Average temperature and its parameter function in respect to a run order.

4. Influence of spray parameters on particle velocity and temperature

Table 16: Indices of parameter levels and summarized parameter functions.

Run order	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Run	13	8	14	9	6	4	2	10	16	12	17	7	3	1	18	11	5	15
Net energy, E	0	1	0	1	0	0	-1	-1	1	-1	1	1	-1	-1	1	-1	0	0
Spray distance, D	-1	-1	1	1	0	-1	0	0	1	1	0	0	-1	1	-1	-1	1	0
Main gas flow rate for velocity, Mvel	-1	0	0	1	1	-1	0	-1	-1	1	0	-1	1	-1	1	0	0	1
Main gas flow rate for temperature, Mtemp	1	0	0	-1	-1	1	0	1	1	-1	0	1	-1	1	-1	0	0	-1
E+D+Mvel	-2	0	1	3	1	-2	-1	-2	1	1	1	0	-1	-1	1	-2	1	1
E+D+Mtemp	0	0	1	1	-1	0	-1	0	3	-1	1	2	-3	1	-1	-2	1	-1

The parameter function was just the sum of indices assigned to the particular parameter levels and normalized by a suitable coefficient to approximately match the range of relative average velocity or temperature curves. Indexing of parameter levels resemble a signum function. The value of a parameter level was indexed 1 or -1 when the change in this parameter as compared to a central level contributed to increase or decrease in the given characteristic (velocity or temperature), respectively. The values of central levels were indexed 0. All indices together with the summarized functions for both the velocity and temperature are listed in

Table 16. From the normalized plots of these functions (open markers, E+D+Mvel in Fig. 4.9 and E+D+Mtemp in Fig. 4.10) it can be seen that the suspicious behavior of the average velocity and temperature, at the beginning of the curves plotted in respect to the run order, is purely the consequence of the combined influence of input plasma spray parameters and the randomization process involved.

From both experimental designs it can be concluded that the particle velocity and temperature could be significantly changed by a selection of the spray parameters.

4. Influence of spray parameters on particle velocity and temperature

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Dominant influences of three of the spray parameters, namely the net energy, spray distance and main gas flow rate, were shown. The effect of increasing net energy and decreasing spray distance on increase of both, the particle in-flight velocity and temperature was observed. An increase in the main gas flow rate led to the increase in the particle velocity and decrease in the particle temperature. As for the carrier gas flow rate existence of the optimal value, at which the powder particles attain maximum velocity and temperature, was shown. Increase in the auxiliary gas flow rate resulted in increase of the particle in-flight velocity, while the influence on the particle temperature was not observed for given plasma gas compositions. Existence of any explicit influence of the powder feed rate on the particle velocity and temperature was, probably due to the low values for powder loading effect, not revealed by any of the experimental designs employed (i.e., “several parameters, one at a time” method and Taguchi design of experiments).

5. PLASMA SPRAYED SPLATS CHARACTERIZATION

Based on the results of previous experiments, three different sets of spray parameters, resulting in significantly different in-flight characteristics of powder particles impacting the substrate surface, were compiled. Since it was shown that the particle velocity and temperature are closely correlated and temperature is harder to control, the difference in the particle velocity was of a greater interest. Plasma spray parameter sets, at which powder particles of zirconia and alumina were deposited onto prepared substrates, are listed in Table 7. For zirconia, two different powder particle size ranges of $(20 - 45) \mu\text{m}$ and $(45 - 75) \mu\text{m}$ were used. In case of alumina, only one particle size range of $(20 - 45) \mu\text{m}$ was available. Mirror-polished square substrates of 316 L stainless steel, at room temperature, were used for splat deposition. The measured particle in-flight velocities and temperatures, for different sets of parameters, at the point of impact are listed in Table 17. The average temperatures of zirconia powder particles never reached the material melting point which is about 2700°C . On the contrary, the measured average particle temperatures for alumina powder were always higher than the melting point of 2050°C .

The plasma deposited particles were observed by optical and electron scanning microscopes. Optical microscopy enables preliminary observation of the sprayed area, especially the amount of adhered material, at low magnifications with a very high contrast. In the optical microscope images every small particle of the ceramic material is clearly seen as a black spot. This is caused by the good reflectivity of the polished steel

substrate as compared to the coating material, resulting in the high contrast images. The depth of focus of optical microscope is very low; it means that when focusing for example on the substrate surface, three-dimensional particles or splats appear blurred. A scanning electron microscope (SEM, JEOL-JSM 5600LV), with larger depth of focus, was used to observe the deposited particles and their morphology at high resolution and high magnification.

Table 17: Velocity and temperature of particles for splat deposition (see Table 7 for spray parameters 1-3).

Set number	Average velocity (m/s)	Average temperature (°C)
YSZ powder (45-75) microns		
1	105	2363
2	137	2398
3	154	2455
YSZ powder (20-45) microns		
1	123	2438
2	144	2427
3	180	2529
Alumina powder (20-45) microns		
1	199	2486
2	241	2967
3	271	2542

5.1 YSZ splats, particle size (45 - 75) μm

The SEM pictures of YSZ powder particles of size of (45 – 75) μm, deposited under the different plasma spray conditions, are shown in Fig. 5.1. No disk-shaped splats with rounded rim without splashing were observed. All the splats have some degree of splashing. When spraying with the low velocity parameter set 1, there were many partially

5. Plasma sprayed splats characterization

Fig. 5.1: SEM pictures of YSZ (45-75) μm deposited with the parameter set 1 (a-b), 2 (c-d) and 3 (e-f).

melted particles observed on the sample surface. Only few flattened particles were found to be adhered to the substrate surface. These particles were thick and not highly spread (Fig. 5.1a). The sample surface was found to be covered by particle debris and to possess some “craters” with imprints of unmelted particles. With the increasing particle impact velocity, highly splashed single splats, sometimes resembling a spider web, were formed. Such splats comprise of relatively compact small center and periphery regions with long projections of splat material (Fig. 5.1c). At the periphery of the central area, the indented shapes were found (wrinkles) that are probably result of the splat solidification before the spreading is completed. According to [68] this entrainment phenomenon may be due to a thermal or chemical gradient in the liquid during the flattening stage on a cold substrate, leading to a finger formation. No cracking of the splat central area was observed for the first layer of splats. The obvious crack network was formed in the second layer of splats impacting on already solidified YSZ splats.

At the highest velocity, splats are also splashed (Fig. 5.1e-f) with the finger projections poorly adhered to the substrate. However, splat finger projections are not so large. Due to the higher velocity of spreading, no wrinkles on the periphery of the central splat area were observed. A number of very small disk-shaped splats were found on the sample surface. This can be caused by powder particle disintegration during the flight. The sample surface was covered with a lot of debris and fractions of splat or splat fingers indicating rebounding of the impacting particles. As compared to splats prepared with spray parameter set 2, splats deposited at the higher velocity and temperature (set 3) contain some cracks due to the stress relaxation after solidification. This indicates that

the higher velocity and temperature resulted in the better adhesion of deposited splats.

5.2 YSZ splats, particle size (20 - 45) μm

When the particle size was reduced to (20 - 45) μm , the in-flight particle temperature increased only slightly – less than 100 °C, probably due to the low thermal conductivity of zirconia. However, the particle impact velocity increased significantly for all the parameter sets used. The SEM pictures of deposited YSZ powder particles with the size range of (20 - 45) μm are shown in Fig. 5.2. For the lowest velocity parameter set (Fig. 5.2a), splashed splats, predominantly those with only short fingers at the rim, were observed. Although, few splats resembling disk shape were found. For this set of parameters, another sample was prepared at the spray distance of 150 mm. The particle impact velocity was 101 m/s and the average temperature of 3153 °C was measured. Better melting of powder particles due to the increased spray distance was confirmed since only the highly splashed splats resembling spider webs were found on the sample surface (Fig. 5.2b). The spray distance was probably increased too much, because on the sample surface a lot of craters with imprints of smooth particles were found, indicating that some particles melted and resolidified during their flight towards the substrate.

With increase in the particle in-flight velocity (parameter sets 2 and 3), more splashed splats were observed with longer material projections at their periphery (Fig. 5.2c). Due to the higher particle temperature, as compared to bigger YSZ particles, no indentation shapes formed by a melt flow over the solidified spots were observed. At

5. Plasma sprayed splats characterization

Fig. 5.2: SEM pictures of YSZ (20-45) μm deposited with the parameter set 1 and spray distance of 50 mm (a), 1 with spray distance of 150 mm (b), 2 (c-d) and 3 (e-f).

the highest velocity, splats are highly splashed with long fingers. With the higher impact velocity, particles spread more and thus after fast cooling (providing good contact with the substrate) a higher stress can arise. The crack network was observed in few splats as a proof of stress relaxation. Some of the splats adhered poorly to the substrate that could cause drop off of the whole splats or their parts (Fig. 5.2e-f).

5.3 Alumina splats, particle size (20 - 45) μm

In case of the alumina powder with the particle size range of (20-45) μm , velocities were much higher than those for zirconia and temperatures seemed to be sufficient for complete powder particle melting prior to impact onto the prepared stainless steel substrate. Since velocities achieved during plasma spraying of the alumina powder were too high, as compared to those obtained for YSZ powders (see Table 17), another sample sprayed at low net energy of 4 kW was prepared. Powder particles sprayed at such conditions reached 2397 °C and the velocity dropped to 89.7 m/s. The amount of adhered particles was lower than for other alumina samples. The deposited particles did not flatten well and formed thick hemispherical objects (Fig. 5.3a), which indicates insufficient melting of particles in spite of the average measured temperature being higher than the alumina melting point. Insufficient melting of powder particles is also evident from sharp notches in the substrate surface, denoting that the particles did not melt and retained its original irregular shape.

As for the regular spray parameter sets, the splat morphology changed from

5. Plasma sprayed splats characterization

Fig. 5.3: SEM pictures of alumina (20-45) μm deposited with parameter set 1 using 4 kW (a), parameter set 1 (b), 2 (c-d) and 3 (e-f).

the disk-shaped to highly splashed. From SEM pictures, it is obvious that the disk-shaped splats adhered well to the substrate or previously deposited splats, and also conformed to the underlying splat shape without splashing. When using the parameter set 2, the particle velocity and temperature increased and the disk-shaped splats start to contain material projections at the rim of the splat (Fig. 5.3c-d). For the high velocity set of parameters 3, obtained splats are highly splashed with low adhesion to the substrate surface (Fig. 5.3e-f). Debonding is indicated by many radial projections that remained bonded to the sample surface when the remnants of the splat de-adhered and dropped off from the substrate.

Generally, images from the optical microscope were used for the first observation of the deposited particle patterns. Due to the big difference in reflectivity of the polished substrate and the ceramic particles, the sprayed areas under the shielding plate orifices were clearly distinguished at low magnifications. In Fig. 5.4 (a-YSZ, b-alumina) a border between the area underneath the orifice and the area shielded by the plate is very obvious. It can be seen that specimen surfaces are heavily covered by plenty of small, mostly spherical particles. These particle fractions are represented in pictures by small black spots and their content increases with the particle in-flight velocity. Larger black spots are supposed to be partially melted or unmelted bigger parts of fragmented particles. The overall amount of debris material adhered to the substrate surface increased with increase in the particle impact velocity. This is caused by improved deposition efficiency of impacting material. Also, a contribution of the splat splashing to the debris content must be taken into account.

The small rounded particles are supposed to result from a rapid melting of the surface and a bad thermal conductivity of YSZ particles. Powder particles start to melt from the surface and due to their low thermal conductivity a layer of melted material is formed. A big difference in the velocity between the particle and the plasma jet results in the disintegration of the particle material and formation of small droplets in the plasma jet. Due to their small heat content, these particles may or may not solidify before impacting the substrate surface. In case of alumina, the substrate surfaces were not covered that much, probably due to the lower melting temperature and better thermal conductivity.

It was later shown by the SEM analysis, that some of the bigger black spots, revealed by the optical microscopy, are craters in the substrate surface. This confirms the presence of hard and fast, unmelted or melted and re-solidified particles in the plasma spray. Unmelted particles can be the result of insufficient melting of particles when travelling in the plasma jet or the particle trajectory in the peripheral region of the plasma spray. During particle deposition, the spray gun was moved from the bottom to the top of the specimen, and thus, it was impossible to eliminate particles from a plasma jet periphery to impact the substrate surface. When any of these hard and fast particles impact the substrate surface, a small crater, with the impression of a particular particle surface is formed. Craters with the surface morphology similar to that of the original powder particles were observed for most of the zirconia samples. Some craters with a smooth surface were observed for smaller zirconia particles, indicating better melting of smaller particles. As for the alumina, angular imprints of the original powder particles

were observed only for the additional set of parameters when melting of powder was very poor.

The optical microscopy also proved to be useful when observing the areas under rebounded splats or their parts. Many thermally affected areas with spots of different colour, due to the changed surface chemistry, than the rest of the substrate, aligned in a circular symmetry, were found (Fig. 5.4c). These indicate that some particles rebound after their impingement and flattening. Rebounding of the central part of the splat is demonstrated by the fingers of the splashed splat still adhered to the substrate surface, while the central part of the splat, usually with some portion of the splat fingers, is missing (Fig. 5.4d). Less of these features were observed for the alumina than for zirconia samples.

After the impact of unmelted or re-solidified particle on the substrate surface, particle kinetic energy is not completely transformed by elastic and plastic deformation of the substrate surface and the particle itself or changed to the thermal energy. These particles spring back and can be found in the sample holder. This was observed by using a sticky carbon tape pasted at the bottom of the holder, where rebounded particles were collected. The significant influence of the in-flight particle velocity and temperature was observed; especially with the higher particle velocity, the amount of rebounded particles was lower. This supports the afore-mentioned idea that with the lower particle velocity, the amount of material adhered to the polished substrate was lower, while the amount of rebounded material was higher under the conditions of the constant powder feed rate.

Typical SEM picture of zirconia rebounded particles is shown in Fig. 5.4e.

5. Plasma sprayed splats characterization

Fig. 5.4: Selected features. Optical micrographs - area under the shielding plate orifice: (a) YSZ, (b) alumina; substrates after splat rebounding (c-d). SEM - YSZ rebounded particles (e), YSZ splat spreading (f).

The particles shown have the same surface structure as the particles of the original powder. Particles can break during their collisions with the substrate surface into smaller pieces. Those particles can be easily distinguished because of their irregular shape. Sometimes particles are melted to some extent, they flatten after impingement on the substrate, but their bonding with the substrate is insufficient and they subsequently drop off from the substrate. Such particles are of an irregular shape with one flat side or they just resemble pieces of splat.

More or less splashed splats were obtained by deposition of YSZ powder particles under the different spray conditions onto the stainless steel substrates at room temperature. Splashing is probably due to the presence of adsorbates/condensates on the substrate surface that disrupt the particle spreading and decrease the contact between the splat and substrate. Improved splat-substrate contact and reduced thermal contact resistance at the interface can be achieved by pre-heating of the substrate, when adsorbates/condensates evaporate. Prolonged heating of a metallic substrate, however, leads to the formation of an oxide layer, which may lead to increased thermal contact resistance as the thickness of the oxide increases [184].

Splats resembling spider webs were obtained for some zirconia samples. They have a relatively compact center as compared to the peripheral area of the splats where a lot of fingers of splashed material can be found. The central part of the splat undergoes contraction and recoils backwards leading to the raised rims around the splat center. At the periphery of the central area the indented shapes were found (wrinkles). Aside from those formed due to the collision with obstacles on the substrate surface, they are

probably result of the solidification of the splat bottom before the spreading is completed and melt flow over the solidified spots. The rest of material with poor contact, due to the low wetting, to the substrate continues in rapid spreading. From time to time, bonds with the substrate are formed by solidification in small localized regions that slow down the spreading and contribute to cooling of the spreading material. The formation of these bonding regions is related to the surface unevenness of the polished substrate (Fig. 5.4f). At the end of the spreading process small particulates can be separated from the splat and later on smeared off on the substrate surface.

Solidification, and thus bonding to the substrate, is strongly dependant on the particle spreading velocity and wettability (contact angle) of the substrate by a liquid material. Wetting has an important influence on the development of the contact between the lower surface of the splat and the substrate surface. Thus, it affects the value of the contact heat transfer coefficient which determines the rate of heat transfer from the splat to the substrate. The value of this coefficient decreases with an increase in the contact wetting angle, which leads to a decrease in the velocity of the splat solidification. It was shown [185], that the increase in the wetting angle causes the increase in the splat thickness and the decrease in the splat radius. The wettability is also related to liquid viscosity and thus to its temperature. The influence of the wetting angle on the flattening process also decreases with the increase in the velocity of the droplet impingement onto the substrate surface. This can be seen from change in splat morphology in Fig. 5.3 where increase in the particle velocity of alumina particles suppressed the influence of the substrate wetting.

The wetting of the substrate by YSZ particles, and thus their mutual contact, was generally very poor. This is confirmed by the presence of “empty” regions on the substrate surface surrounded by the splat material fingers and formation of only a small number of bonding zones with the substrate. Better wetting of the substrate was observed for alumina particles forming continuous disk-shaped splats. Due to the better contact with the substrate, adhesion of the particles was improved as indicated by the formation of the dense crack network. The cracking occurs after the solidification is completed due to the splat cooling accompanied by thermal contraction and possible phase transformations. The splat cools down from much higher temperature than the substrate and hence the splat contracts more than the substrate that serves as a constraint. As a result, tensile quenching stresses rise in the splat. When the quenching stress in the splat reaches the tensile strength of brittle ceramics a vertical crack develops across the splat thickness to relieve the high stress. Cracking occurs almost simultaneously at different locations leading to formation of the crack network and crack-free segments [226].

5.4 YSZ and alumina powders plasma sprayed into water

In order to investigate the degree of melting of the particles during their transfer towards the substrate, alumina and YSZ powders were plasma sprayed into the container filled with water. The same plasma spray conditions as for the splat deposition were used (Table 7). Spraying was conducted into “still” water, it means without any additional stirring. However, the plasma jet with the stream of particles caused significant movement and splashing of water during spraying. Spray time was about two minutes in

order to obtain enough powder for subsequent analysis. The angle between the longitudinal axis of the spray gun and still water level at the beginning of spraying was approximately 60 degrees and the spray distance was 150 mm. After spraying and powder sedimentation, the excess water was decanted and the sediment powder was dried in an oven at temperature of 50 °C for 12 hours. Powder particle surfaces and cross-sections were observed by SEM, possible phase changes then by Raman spectroscopy (Renishaw RM 1000, HeNe 633 nm) and X-ray diffraction analysis (Philips PW 1830/00, Cu K α 1 λ =1.54 nm).

5.4.1 SEM analysis of YSZ powders

The SEM pictures of YSZ powder particles with the size range of (45 – 75) μ m after the plasma spray into water and drying are shown in Fig. 5.5. In all cases, the particles with melted, un-melted and partially melted surfaces were observed. From the pictures, it is evident that the higher the net energy, the most influential parameter on the particle in-flight velocity and temperature, the better the melting of the powder particles. When using the low energy set of parameters, most of the powder particles show the same morphology of sintered particles as the original powder. A small portion of particles, especially those smaller in size, carry some traces of surface melting during the plasma spraying. The insufficient melting for the powders sprayed at low net energies can be caused also by a low thermal conductivity of YSZ and a short time in the plasma jet given to the powder particle to be properly heated. With the increasing spray net energy, more and more particles show some degree of the surface melting. Finally, with

5. Plasma sprayed splats characterization

Fig. 5.5: Surface and cross-section SEM pictures of YSZ powder plasma sprayed into water, particle size (45-75) μm: parameter set 1 (a-b), 2 (c-d) and 3 (e-f).

the highest net energy used, most of the particles seem to be melted - if not totally to their core then at least to some depth from their surface. This confirmed improved heating of the particles in the plasma jet.

Apparently, it is not enough to infer the particle's degree of melting only from the observation of the particle surface. It can happen that a particle with smooth surface, which seems to be melted, could be melted only on its surface with the core remaining solid. In the SEM pictures of the powder cross-sections, three kinds of particles can be found (Fig. 5.5). First, unmelted particles with the same microstructure as particles of the original powder. The powder particles were agglomerated from smaller pieces during a powder preparation process. Their cohesion is very poor and very often small pieces of the particles crumble away during polishing. This leads to an uneven surface of sectioned particles evident from the pictures.

Very similar to unmelted particles are partially melted ones. The difference is that the partially melted particles are separated from a surrounding resin by a ring of compact material as a consequence of melting and solidification of the particle surface layer. The cohesion of the ring material is much better than that of the core of particle and that is why this ring can be polished and clearly distinguished. These particles have a smooth surface and thus they cannot be recognized from the fully melted particles when observed only from the surface. Sometimes, the ring is not closed or the melted and solidified material represents only a small part of the powder particle. Such particles correspond to those with the partially melted surface in the SEM surface observation.

Lastly, there are the melted particles. These are composed of melted and solidified

material with a good cohesion and are demonstrated by the planar circles in the SEM pictures. Sometimes, these particles contain hollow spheres. Note that these hollow spheres can participate in the overall coating porosity which is sometimes desired and sometimes detrimental. Presence of a hollow sphere inside the particle is a proof of good particle melting during the plasma spraying. The formation of hollow spheres will be discussed later.

The degree of melting of plasma sprayed YSZ powders was determined through the image analysis of sectioned powder particles. SEM pictures captured at magnification of 300x were used for the particle diameter measurements. The ‘melt fraction in particle’ (*MFP*) was defined in [187] as the ratio of the particle melted volume to the whole particle volume and calculated according to the following formula:

$$MFP = \frac{V_{p,melted}}{V_{p,total}} = \frac{R^3 - r^3}{R^3} \times 100\% \quad (13)$$

where R and r are the radii of the powder particle and potential unmelted core, respectively. $V_{p,melted}$ and $V_{p,total}$ correspond to the melted and total volume of the particle, respectively. More than hundred particles were inspected for each powder. Calculated average values of *MFP* for YSZ powders plasma sprayed under different plasma spray conditions are in Table 18. The error of measurement was less than 5% except for the powder with the lowest *MFP* for which the error was higher than 7%. Results revealed that the average *MFP* of YSZ powders increased more than two times with the increase in spray net energy from 37.7 % to 78.2 %.

Table 18: Average ‘melt fraction in particle’ (*MFP*) and ‘melt fraction’ (*MF*) for YSZ powders plasma sprayed at different conditions.

Parameter set	MFP (%)	MF (%)
1	37.7	23.1
2	50.7	36.2
3	78.2	69.3

Fig. 5.6: Powder particle *MFP* as a function of the particle diameter for YSZ powders prepared under different spray conditions.

The SEM pictures of plasma sprayed YSZ powders demonstrate the miscellaneous powder melt states. The *MFPs* of individual particles as a function of the particle diameter are plotted in Fig. 5.6. It is obvious that the melt fraction of the particles decreased with an increase in the particle size. It can be also seen that with the increase in spray net energy the melt fraction of particles of the same size increased and also that more of the bigger particles become melted.

Since the particles that seem to be fully melted in the SEM pictures ($MFP=1$) can be, partially melted particles sectioned at their periphery, 'melt fractions' (MFs) of sprayed powders were also determined as ratios of the overall amount of melted material to the total amount of material:

$$MF = \frac{V_{melted}}{V_{total}} = \frac{\sum V_{p,melted}}{\sum V_{p,total}} \quad (14)$$

Results of average MFs are also listed in Table 18. MF of the YSZ powders increased three times with increasing spray net energy, however, the particular values are lower as compared to MFP . Assuming the ostensibly fully melted particle (as appears in the SEM picture) to be fully melted leads to an artificial increase of the average MFP when this particle is, in fact, partially melted and sectioned at its periphery. That is why the values of MFP and MF differ more for the less melted powder. Also easier melting of the smaller particles results in an increase of the average MFP . Using MF , where errors due to the particle sectioning are statically balanced off, eliminates such phenomena.

5.4.2 SEM analysis of alumina powders

The melting of the alumina powder particles, irregular in shape, on the contrary to the spherical particles of YSZ, during the plasma spraying is indicated by the particle spheroidization. As can be seen from the SEM pictures in Fig. 5.7 the degree of melting of the powder particles increased again with the increasing net energy. The melted particles, spherical in shape and with a smooth surface, can be easily differentiated from the unmelted angular particles. One interesting aspect is the presence of rounded particles

with a specific surface morphology. These are assumed to be partially melted particles. Their indented surface is supposed to be the result of bundling of the particle material when adopting the spherical shape due to the melting in the plasma jet and of high plasma velocities. In all cases, the average powder temperature was above the melting point of alumina (see Table 17). Therefore, most of the unmelted angular particles found in powder samples, especially in those sprayed at the highest net energy, are attributed to frequent powder saltation. Accordingly, quantifiers such as *MFP* or *MF* for the powder melting determination could not be used due to the powder saltation, an uncontrolled phenomenon. Powder saltation was result of bad flow characteristics of alumina powder in a feed hose. The cross-section observations of alumina powders could not help to differentiate between the melted and the unmelted portion of particles. The alumina powder was not prepared by sintering and agglomeration, as in the case of YSZ, but by crashing big alumina pieces into the smaller ones. Thus, compact unmelted particles also gave a smooth surface after polishing. The only indicator of melting of the powders was the spheroidization of the particles which was observed from previous SEM analysis.

However, observation of the cross-sections revealed the existence of a number of hollow spheres inside the spherical powder particles. The amount of hollow spheres was higher for the powders sprayed with higher net energy parameter sets.

The ease with which the powder particle is melted in the plasma jet is characterized by the heat content per unit volume of liquid at melting point. Heat transfer is predominantly by conduction through the surface boundary layer and it depends on

5. Plasma sprayed splats characterization

Fig. 5.7: Surface and cross-section SEM pictures of alumina powder plasma sprayed into water: parameter set 1 (a-b), 2 (c-d) and 3 (e-f).

the gas properties in the jet. In spite of the “difficulty of melting factors” being similar for zirconia and alumina [168], from the observations it is concluded that the melt fraction is higher for alumina powders for the same set of spray conditions. Also measured temperatures higher than the alumina melting point that is lower than the one of zirconia and powder of smaller particle size used are sound arguments supporting this conclusion.

A lot of hollow sphere particles were found in the plasma sprayed YSZ and alumina powders. The presence of a hollow sphere in the sprayed powder particle is a proof of good particle melting during the plasma spray process.

Assume a melted spherical particle. If the cooling of the particle is spherically symmetric, a solid layer grows at the entire particle surface. Since the mass density of the solid phase is higher than the density of the melted one, the hydrostatic pressure in the melted phase decreases. According to the Clausius-Clapeyron equation, the boiling point temperature decreases with the pressure decrease. In fact, the pressure of the melted phase can even reach, for a moment, negative values at early stage of the solidification. Therefore, a bubble arises in the region of the highest temperature of the melt. The bubble born in a region of inhomogeneous temperature will move towards the temperature maximum [186], [188].

Another explanation of hollow sphere formation is given in [189] for agglomerated powder particles. Spray dried agglomerate, with inherent porosity, melts in the plasma and gas in the outer layer of the agglomerate escapes, whereas gas in the centre of the agglomerate is trapped within a molten shell. An experiment, using yttria, showed

that the relative size of the pore was dependent on the particle diameter. It has been proposed that the major controlling factor that influences this dependence is the escape of gas trapped in the spray dried agglomerate during the melting (melted outer layer thickness, material melting range).

5.4.3 Raman spectroscopy

The Raman spectroscopy is an important method for the elucidation of a molecular structure, for locating various functional groups and chemical bonds in molecules. Raman spectra are acquired by irradiating a sample with a powerful laser source of visible or near-infrared monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at some angle (often 90 deg) with a suitable spectrometer. At the very most, the intensities of Raman lines are 0.001 % of the intensity of the source; as a consequence, their detection and measurement are somewhat more difficult.

If one or more of the normal modes of vibration of a molecule involves changes in the polarizability (polarizability describes a molecular property having to do with the deformability of a bond), then the scattered radiation contains this vibrational frequency superimposed upon the frequency of the incident radiation. Actually, the scattered wave contains three frequencies, that of the incident radiation and the incident radiation frequency plus and minus that of the Raman-active vibration. The intensity or power of a normal Raman peak depends in a complex way upon the polarizability of the molecule, the intensity of the source, and the concentration of the active group, as well as other factors. Raman intensities are usually directly proportional to the concentration of the active species [190], [191].

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5. Plasma sprayed splats characterization

In the present experiment, Raman spectroscopy was used to investigate whether phase changes in zirconia and alumina particles occur after heating during the plasma spraying and subsequent rapid cooling in water. First, Raman analyses of powders with known phase content were done and the resulting spectra were compared with the spectra obtained for powders after the plasma spraying. Following powders were available for YSZ:

- 100% ZrO_2 , monoclinic phase, particles with an average size of 70 nm were dried from solution, disperser used to spread particles in solution resulted in a strong background in Raman spectra
- $\text{ZrO}_2 + 3 \text{ mol.}\% \text{ Y}_2\text{O}_3$, partially stabilized, tetragonal phase
- $\text{ZrO}_2 + 10 \text{ mol.}\% \text{ Y}_2\text{O}_3$, fully stabilized, cubic phase

The typical Raman spectra of these powders together with spectrum of powder used for plasma spray, containing 8 wt. % (4.5 mol. %) of Y_2O_3 , are shown in Fig. 5.8. In all evaluations of the Raman spectra obtained, information about Raman peaks of YSZ obtained from various sources ([192], [193], [194], [195], [196], [197]) were taken into account.

From the diagrams shown, it is obvious that the starting powder is very similar to the one with 3 mol.% of yttria, thus it should contain mostly the tetragonal phase. However, according to the presented references, the double peak below Raman shift value of 200 cm^{-1} is typical for the monoclinic zirconia phase. In the spectrum of pure zirconia, these peaks could be suppressed by a strong background coming from a

dispenser. Another proof of the monoclinic phase in the starting powder is the peak around 550 of Raman shift. The peak at Raman shift of 500 cm^{-1} can arise, according to references, from all three zirconia phases, so it does not provide any additional information about the phase content of the starting powder.

Fig. 5.8: Raman spectra of the starting powder (4.5 mol. % of yttria) and powders containing 0, 3 and 10 mol. % of yttria.

As it was shown, particles with various degree of melting were found in powders plasma sprayed into water. Correspondingly, obtained Raman spectra were more or less similar to that of the original YSZ powder. Apparently, the result of the Raman analysis depends on the selected particle, the location on its surface as well as the particle orientation. For all the analyses done, typical spectra obtained from un-melted and melted zirconia particle surfaces are shown in Fig. 5.9. The peaks were, according to the

5. Plasma sprayed splats characterization

obtained information from references, assigned by letters *c*, *t*, *m* representing cubic, tetragonal and monoclinic zirconia phases, respectively.

Fig. 5.9: Raman spectra of the starting YSZ powder, un-melted and melted particle after the plasma spraying (*c*, *t*, *m* indicate cubic, tetragonal and monoclinic phases respectively).

From spectra comparison, it can be seen that the spectrum of an un-melted YSZ particle contains the same peaks as the spectrum of the original powder, only relative intensity ratios of peaks are different. Monoclinic peaks are more intensive than the peaks for tetragonal phase, which indicates that the tetragonal phase transformed to the monoclinic one. The plasma spraying, without material melting, was in this case only an additional heat treatment of original powder particles enabling this kind of phase transformation. On the other hand, Raman spectrum of melted particle is significantly different from that of the starting powder. Some peaks were suppressed, some completely

disappeared, which indicates phase transformations. In this spectrum only two strong peaks, around Raman shift of 255 and 638 cm^{-1} , can be found. Both of them represent the tetragonal phase. It means that after particle melting and subsequent rapid cooling in water, the tetragonal phase was retained in powder particles. Broadening around these peaks indicates existence of the amorphous material as well.

Available powders with known phase contents for alumina were:

- Original Al_2O_3 powder containing alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) phase only
- Al_2O_3 powder, 99.997 % gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) phase

In comparison with the Raman spectra obtained for zirconia powders, spectra for alumina powders are very simple, showing just a single peak or double peak for gamma or alpha alumina phases, respectively. The alpha alumina phase should be characterized by a strong double peak at around Raman shift of 1400 cm^{-1} (Fig. 5.10). The gamma phase in the second powder available is represented by a peak at around 519 cm^{-1} of Raman shift in its spectrum.

The Raman spectra of the different particles from powders plasma sprayed into water were analysed and compared with the reference peaks obtained for alpha and gamma alumina phases. No difference in the Raman spectra for the original and the unmelted particles were observed. Spectra of the particles with some portion of its material melted and resolidified showed peaks for both alpha and gamma alumina phases (see Fig. 5.10). The Raman spectrum of the completely melted alumina powder particle shows only the peak for the gamma alumina phase. Preferential formation of

the metastable gamma alumina phase, which has presumably lower nucleation barrier than other alumina polymorphs, is a consequence of melting and rapid cooling of the sprayed alumina powder.

Fig. 5.10: Raman spectra of the original alpha alumina particles, partially and fully melted particles after the plasma spraying.

As it was shown in the SEM pictures of sectioned particles, the particle with a melted surface may not have a melted core. In such a case, the phase content differences would be expected between the particle melted surface and the un-melted core. However, no spectra of the sectioned particles were obtained from available Raman spectroscopy apparatus, even when using the low laser power and different ways of particle cross-section preparations. No results were also obtained for the thin splats prepared on the stainless steel substrates. Differences in the splat phase content could correspond to the

differences in the cooling and solidification rates inside the splat. Once a laser beam was aimed to thicker, partially melted particles adhered to the substrate surface, the spectra were obtained but it never worked on thin portions of splats.

5.4.4 X-ray diffraction analysis

The X-ray diffraction (XRD) analysis was implemented in order to confirm the results indicated by the Raman spectroscopy. Moreover, the Raman spectroscopy is a method based on observations of selected powder particles or their parts while the XRD enables to study the powder sample as a whole. XRD provides information about the phases present based on the differences in their crystal structure. Each crystallographic phase has its own unique diffraction pattern. A mixture of phases produces a superposition of these diffraction patterns, where the peak positions of the individual phases are preserved and the intensities are proportional to the volume percentage of a given phase, modified by the absorption in the other phases. In present study the phase composition was determined using phase weight fractions calculated as relative intensity of selected lines for each phase. This relative intensity was calculated as ratio of the integral intensity of selected lines for each phase and the total intensity of selected lines of all considered phases. Peak profiles were fitted with TBasic software by the least square method employing Lorentz function. More about the quantitative analysis using peak relative intensities can be found elsewhere [91], [92], [93], [94], [95], [96].

The XRD spectra for YSZ (45 - 75) μm powders sprayed into water under different spray conditions are shown in Fig. 5.11. It is obvious, that after the plasma spraying of

YSZ powder into water the amount of the tetragonal phase increased while the amount of
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the monoclinic phase decreased. Intensity of the peaks with 2θ values of 28.15° (-111) and 31.44° (111), representing the monoclinic zirconia phase, decreased. Some of the monoclinic peaks of 2θ values around 24.4° (110), 34.1° (200), 40.7° (-112) and 49.25° (220) totally disappeared. On the contrary, the intensity of peaks representing the tetragonal zirconia phase increased significantly with the increase in the spray net energy, especially the one of 2θ value of 30.15° (101) and overlapped peaks around 50° ((112) and (200)).

In order to determine the contents of monoclinic and tetragonal phases in individual samples, at first, the volume fractions were calculated using the following formulas [98], [99]:

$$v_m = \frac{1,311 \cdot [I_m(-111) + I_m(111)]}{I_t(101) + 1,311[I_m(-111) + I_m(111)]} \quad (15)$$

$$v_t = 1 - v_m \quad (16)$$

where v_x and $I_x(hkl)$ denote the volume fraction and relative intensity of respective peak of phase x . Results of calculations were converted into phase weight fractions and are shown in Table 19.

Results confirmed that heating of the YSZ particles during the plasma spraying and their subsequent rapid cooling in water results in phase content changes. The volume fraction of monoclinic phase in the powders decreased significantly after plasma spraying (by more than 30 %). Less monoclinic phase, and therefore, more tetragonal phase, was found in the powder sprayed at higher net energy. Retention of the tetragonal zirconia

phase to the room temperature is desirable and results in higher toughness and strength of a ceramic material [88].

Fig. 5.11: XRD spectra of YSZ powders sprayed into water under different spray conditions.

Table 19: Weight fractions of monoclinic phase in YSZ powders after plasma spraying.

Sample	$I_m(-111)$	$I_t(101)$	$I_m(111)$	$w_m(\text{wt.}\%)$
Original powder	101.5	358.9	74.6	37.1
Parameter set 1 ~ 6 kW	14.1	395.0	11.5	7.2
Parameter set 2 ~ 10 kW	19.7	576.1	14.3	6.6
Parameter set 3 ~ 14 kW	12.3	598.2	9.5	4.2

XRD spectra of the alumina powders plasma sprayed into water under different spray conditions are shown in Fig. 5.12. In an original alumina powder feedstock, only the thermodynamically stable alpha phase, represented by several peaks, was detected. The strongest peaks are around 2θ values of 25.58° (012), 35.15° (104), 43.36° (113) and 57.50° (116). Alpha phase is usually the most desirable phase in plasma spray deposits

for its high corrosion and erosion resistance and hardness. After the powder plasma spraying into water, peaks representing the gamma phase appeared. The alumina gamma phase is represented mainly by three peaks located at 2θ values of 39.54° (222), 45.94° (400) and around 67.03° (440). The crystalline forms of alumina are constructed of stacked, close packed layers of oxygen ions with aluminium ions and the vacancies distributed on the tetrahedral and octahedral sites within the oxygen ions. The polymorphism results from the possibilities for different oxygen layer stacking sequences and from the variations in the distribution of aluminium ions on tetrahedral and octahedral sites and from the ordering of aluminium ions and vacancies on these sites [104].

From the diagrams it can be seen that intensities of the γ -alumina phase peaks increased, and at the same time the intensities of the α -alumina phase peaks decreased, with the increase in the net energy used for plasma spraying. The volume fractions of α phase in alumina powders were determined using formula:

$$v_\alpha = \frac{RIR_\alpha \cdot [I_\alpha(104) + I_\alpha(113)]}{RIR_\alpha \cdot [I_\alpha(104) + I_\alpha(113)] + RIR_\gamma \cdot I_\gamma(400)} \quad (17)$$

where v_x , $I_x(hkl)$ and RIR_x denote the volume fraction, relative intensity of respective peak and relative intensity ratio of phase x , respectively. Relative intensity ratios of alpha and gamma phases used for calculations were 1 and 0.89, respectively. Calculation results are shown in Table 20.

5. Plasma sprayed splats characterization

Fig. 5.12: XRD spectra of the alumina powders sprayed into water under different spray conditions.

Table 20: Weight fractions of alpha phase in alumina powders after plasma spraying.

Sample	I_{α} (104)	I_{α} (113)	I_{γ} (400)	w_{α} (wt.%)
Original powder	277.1	461.5	-	100.0
Parameter set 1 ~ 6 kW	163.6	187.5	65.9	85.7
Parameter set 2 ~ 10 kW	201.9	240.1	59.1	89.4
Parameter set 3 ~ 14 kW	88.8	141.6	121.3	68.1

It is clear that the fraction of alumina phase decreased in powders after plasma spraying as compared to the original powder containing 100 % alpha phase. The biggest decrease was observed for the highest net energy used indicating the improved conditions for powder melting. Generally, the higher the cooling rate of the molten material the more gamma phase can be formed. Due to the liquid undercooling gamma phase nucleates in preference to alpha phase and the cooling rate after solidification is sufficiently rapid to prevent transformations to delta or alpha phases. The powder

particles sprayed into water are cooled down significantly more slowly than those on a cold substrate (10^4 K/s compared to 10^6 K/s in average). Available time for transformation is longer and sometimes δ -alumina phase forms. Delta phase is also metastable and its peaks are usually overlapped with those of gamma phase (such as (400) peak used in calculations). The transformation of metastable delta or gamma to alpha phase is accompanied by a significant volume change (γ to α volume change is about 15 %), resulting, for example, in microcracks formation in the coatings. The remaining α alumina phase in the powders represents an unmelted fraction of the feedstock material or possibly a small amount of a new α phase formed on the unmelted cores of the powder particles. [89], [90], [106], [107].

SEM analysis of plasma deposited YSZ and alumina single splats showed significant influence of the particle impact velocity and temperature on the splat formation and morphology. Evident increase in the splashing of the YSZ splats with increasing particle impact velocity was observed. In case of the alumina particles the splat morphology changed from disk-shaped to splashed splats with an increase in the particle velocity. Improved particle melting with an increase in spray net energy was demonstrated on powders plasma sprayed into water. The YSZ powder melt fraction, established by image analysis, increased three times with the change in spray conditions. Better powder melting was also indicated by changes in the phase compositions for both types of powders. Raman spectroscopy and X-ray diffraction revealed higher content of the high temperature tetragonal zirconia and metastable gamma alumina phases retained

5. Plasma sprayed splats characterization

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in YSZ and alumina powders, respectively, with increase in spray net energy. Semi-quantitative analysis of XRD data showed drop by more than 30 % in weight fractions of the original zirconia and alumina phases due to the formation of metastable ones with increase in the net energy, indicating better powder melting.

6. PLASMA SPRAYED COATINGS

CHARACTERIZATION

Plasma spray of ceramic powder particles onto metallic substrates is an important process in modifying surface properties of engineered components. It is a versatile technology that has been quite successful for deposition of functional thermal barrier coatings. The produced coatings are formed by agglomeration of individual droplets impacting onto the substrate surface. The coating properties (e.g. thermal diffusivity, porosity, adhesion, cohesion, residual stress), to a large extent, depend on the microstructure of the coating, its formation and resulting quality of interface contacts between the splats and the splats and the substrate. The coating microstructure is, in turn, dependent on the particle impact conditions and the substrate temperature, chemistry and topology.

Yttria stabilized zirconia and alumina coatings were prepared under the different plasma spray conditions. Influence of the different particle impact velocities and temperatures on the final coating thermal conductivity (diffusivity) and porosity was studied. The final coating properties were investigated by XRD, laser flash method, optical microscopy porosity measurement and electrochemical impedance spectroscopy. The porosity values were compared with those obtained by numerical simulation of a coating formation process. Two lots of powders with different particle size ranges of (20 – 45) μm and (45 – 75) μm were used for the preparation of YSZ coatings. Alumina powder with the particle size range of (20 – 45) μm was available. The plasma sprayed

coatings were deposited using spray parameter sets listed in Table 7 with the spray distance set to 100 mm. Due to the requirements of the laser flash method, thick coatings were sprayed and grinded down to thickness of about 1.4 mm. A stress developed during the spraying of such thick coatings resulted in delamination of the coatings from the grit-blasted stainless steel substrates, which was favorable to obtain self-standing coatings.

6.1 SEM observation of as-sprayed coatings

The plasma sprayed YSZ and alumina coatings were observed by the SEM, so as to compare the surface splat morphology. It was expected that splats would differ from those obtained at the polished stainless steel substrates. Main differences in impact conditions are the surface temperature and topography. Whilst the single splats were deposited on the substrates at room temperature, the particles at the top of the thick coatings landed on the previously deposited layers whose temperature, in spite of the heat sink through the substrate, can be in order of hundreds of degrees. Besides, the material properties of the deposited YSZ or alumina layers are different from those of the stainless steel. Topography of the previously deposited layers plays also an important role on a subsequent particle deposition. The effect of topography on the flattening, splashing and cooling of droplets depends on the relation of dimensions of unevenness with respect to the droplet size. As a general rule, the splat thickness increases and the flattening degree decreases with the substrate roughness and, thus, its cooling rate decreases. The material splashing is enhanced by unevenness of previously deposited particles and can lead to formation of porosity and voids as well as to an improper contact between the

adjacent splats. The degree of flattening and splashing and thus coating roughness depends on the impact velocity and temperature of the arriving particle. The coating roughness decreases if the particle velocity and temperature at the moment of impact are greater and increases with the powder particle size. The particle velocity and temperature have also strong influence on filling the voids by the impinging particles. During SEM observations, voids in order of several splat thicknesses in depth were found in the coatings.

The SEM pictures of the YSZ coatings prepared under the different spray conditions are shown in Fig. 6.1 for powder with the particle size range of $(45 - 75) \mu\text{m}$ and in Fig. 6.2 for powder with the particle size range of $(20 - 45) \mu\text{m}$. For each sample, pictures of the top and fractured, by three-point bending, surfaces are shown. It is obvious that for all the coatings the amount of unmelted material is quite high. However, with the increase in net energy in the spray parameter sets (from set 1 to 3) an amount of unmelted material decreased. In the SEM pictures, more areas of melted and solidified material with cracks can be seen. This is in compliance with the results of the examination of the degree of melting in the powder particles plasma sprayed into water. Differences in the ratio of unmelted material and the overall arriving particles agglomeration can be seen also from the pictures of fractured surfaces. It can be postulated that with the change in spray parameters, more particles form the typical lamellar structure of the coating. From the observations, it also seems that the conformity of the splats improved resulting in the better mutual splat contact and the lesser porosity formation. In the pictures of coatings prepared at higher net energies, a lot of fractured splats can be seen (columnar

6. Plasma sprayed coatings characterization

Fig. 6.1: SEM pictures of the top and fractured surfaces of YSZ coatings prepared by deposition of powder with the particle size range of (45 – 75) μm : parameter set 1 (a-b), 2 (c-d) and 3 (e-f).

6. Plasma sprayed coatings characterization

Fig. 6.2: SEM pictures of the top and fractured surfaces of YSZ coatings prepared by deposition of powder with the particle size range of (20 – 45) μm: parameter set 1 (a-b), 2 (c-d) and 3 (e-f).

structure). All the features described were the same for both lots of powder. Better melting of the powder together with the smaller particle size, in case of coatings prepared from (20 – 45) μm powder, resulted in coatings with a lower content of unmelted material as compared with corresponding coatings prepared under the same conditions from the powder with the particle size range of (45 – 75) μm .

The SEM pictures of the top and fractured surfaces for alumina coatings are shown in Fig. 6.3. In case of the alumina powder, the particle impact temperature was far above the melting point of alumina, for all sets of the spray parameters, resulting thus in a good degree of melting. Therefore, nice splats can be clearly observed on the top of all the coatings. Increase in the particle impact velocity and temperature due to the increase in net energy enhanced the droplet splashing as can be seen from the pictures of top surfaces. Irregular areas in the picture of the sample surface prepared with net energy of 14 kW are attributed to the droplet splashing, not to the unmelted material deposition as in case of the zirconia coatings. In all the pictures of the fractured surfaces, a clear lamellar structure formed by individual splats can be seen. The first two pictures show some splat surfaces as a result of an intersplat fracture. On the contrary, a sample prepared at the highest spray net energy shows more of the intrasplat fracture, suggesting an improved contact between the splats and evolution of vertical cracks. The vertical cracks develop in coatings due to the stress relaxation in highly spread and well-bonded splats.

6. Plasma sprayed coatings characterization

Fig. 6.3: SEM pictures of the top and fractured surfaces of alumina coatings: parameter set 1 (a-b), 2 (c-d) and 3 (e-f).

6.2 Porosity evaluation of YSZ and alumina coatings

During the coating build-up, powder particles with the different degree of melting and velocity impact the surface of an uneven previously deposited layer which results in development of the porosity in the plasma sprayed coating. Generally, four different defects in the coating microstructure are denominated as porosity (Fig. 6.4):

- pores and voids between the splats (stacking defects, unmelted particles)
- pores inside the splats (condensates and adsorbates or gas entrapments)
- intersplat cracks (horizontal cracks due to a poor contact between the splats)
- intrasplat cracks (vertical cracks due to the stress relaxation or separating individual splats)

Fig. 6.4: Scheme of different defects denominated as porosity.

All conventionally thermal sprayed coatings contain some porosity. The porosity can be caused by low impact energy (unmelted particles or low velocity), shadowing effect (unmelted particles or spraying under an angle) and by shrinkage and stress relieve effects. The coatings have porosity usually from 1 to 25 %. The porosity can be detrimental to many mechanical properties such as strength, hardness and wear

characteristics as well as to a corrosion resistance. The porosity reduces the effective coating thickness. On the contrary, the porosity may also have positive effects on the coating performance as in reducing stress levels, increasing thermal barrier properties, shock resistance properties and lubrication characteristics of frictional surfaces reducing their wear [243], [246].

A number of pores and their size and shape distributions are of great importance in the quantitative description of the porosity. The pores in the plasma sprayed coatings are not distributed uniformly but have a layered structure. Thermal spray deposits are considered to be transversely isotropic with respect to the spray direction. These distributions can be determined by a stereological analysis. Stereology deals with estimates for describing a three-dimensional space, when only two-dimensional sections through this space are available. It attempts to numerically characterize features of the two-dimensional sections and to establish the relationships with those features in the three-dimensional space. The rules of these estimates are based on geometric probabilities. The slip plane cannot pass through the centers of all the features, and hence, the diameter of two-dimensional features, and estimated characteristics (e.g. porosity) on their basis, will always be less than those of the real ones. Various kinds of objects with different shapes are encountered in coating microstructures (i.e. splats, unmelted particles, particles from splashing, pores and cracks) and are often assumed as certain geometrical shapes such as spheres, ellipsoids, cubo-spheres and cubes to determine the size and/or shape and their distributions [242]. Splats, pores and cracks can be approximated to spheroids. Spheroids, that is, ellipsoids of revolution, can approximate

many of the shapes encountered in thermal spray deposits. Two basic morphologies can be considered, the prolate particle and the oblate particle, respectively, generated by rotation around the major axis, a , and around the minor axis, b , of an ellipse [240], [241], [242], [249]. An approximation of two-dimensional cross-section of a pore to a circle, the size of which was evaluated by its diameter, was used in [243].

Semi-quantitative technique for the porosity assessment is an image analysis of the optical microscopy or SEM pictures of coating polished cross-sections. Commercial software, involving the different algorithms to extract particular features from the pictures (noise reduction, filtering, binarizing) and the selection of proper threshold value, is usually used to perform an image analysis. Porosity of the coating is obtained by dividing the calculated area of pores by the total image area [244], [247], [248].

In this study, porosity of YSZ and alumina coatings was determined by a point count method using optical microscopy images. The metallographic preparation was identical for all the coatings and is described in section 3.4. In total, about 30 pictures at magnification of 400x were captured for each sample by a digital camera attached to the optical microscope. The acquire sequence of optical microscopy images started at the side of former interface with the substrate of the sectioned sample and went four times through the sample thickness towards the other end of the sample. The image acquire design within a coating sample is schematically shown in Fig. 6.5. The acquired images were analysed by the Image-Pro Plus software. After calibration, the threshold value settings were optimised and the same procedure was used for the analysis of every image. The area of porosity determined by a point count method was then divided by the total

area of the image and the porosity was expressed as a percentage value.

Fig. 6.5: Image acquire design for the porosity determination.

The average values of measured porosity (see Table 21) plotted against the parameter set numbers for all the coating samples are shown in Fig. 6.6. From the diagram, it is obvious that the porosity of the coatings decreased with the increase in the spray net energy. With the increasing powder particle impact velocity and degree of melting, measured porosity decreased. Higher degree of splashing of the impacting particles, which would contribute to the increase in porosity, was probably outweighed by a better filling of empty spaces, less unmelted particles, better coherence and a mutual contact among splats. The decrease in porosity was also observed when the powder particle size of YSZ powder decreased, probably due to the better degree of melting and the smaller particle size. It is necessary to note that the absolute values of measured porosity do not correspond to the term porosity as defined above. The SEM observations of as-sprayed coatings revealed a lot of unmelted material in the coatings, especially for the YSZ coatings. Such unmelted parts of the coatings, and also splats with a poor mutual contact, have a very low cohesion resulting in the pullouts occurrence during the cross-section sample preparation. Such areas appear black on the optical micrographs and were inevitably included in the counted porosity area. Out of this reason, the absolute values of porosity have to be thought of semi-quantitative; however, qualitatively they show very

well the decrease in the coating porosity with the change in the spray parameters.

Table 21: Average porosity of the coatings determined by a point count method.

Parameter set	Porosity (%)
Alumina powder (20-45) microns	
1	23
2	17
3	14
YSZ powder (20-45) microns	
1	37
2	25
3	20
YSZ powder (45-75) microns	
1	41
2	30
3	20

In Fig. 6.7, Fig. 6.8 and Fig. 6.9 there is the coating porosity plotted against the coating thickness (distance from the substrate-coating interface) for all the three powders. Each point in diagrams represents the average of four values measured at a given distance from the substrate, as indicated in Fig. 6.5. A scatter experienced in data measured at the same distance from the substrate is due to the selective nature of measurement (selected area that was observed and measured can contain large defects) and sample preparation (large pullouts). This scatter, manifested in diagrams by data fluctuations, was reduced by averaging of the four values. Usually the relative error for each point was up to 10 % (not the porosity percent!). There was no trend observed in the coating porosity with increasing distance from the substrate for the zirconia coating samples. It seems that for the alumina coatings the measured porosity decreased with the increasing thickness. This can be caused by different phenomena such as impact of further particles on hot previously deposited layers, improved wettability, inter-splat

6. Plasma sprayed coatings characterization

Fig. 6.6: Average porosity measured by a point count method.

Fig. 6.7: Change in the alumina coatings porosity with thickness.

Fig. 6.8: Change in the YSZ (20 – 45) μm coatings porosity with thickness.

Fig. 6.9: Change in the YSZ (45 – 75) μm coatings porosity with thickness.

contact, coherence and effect of large compressive stresses.

6.3 Numerical model for the porosity assessment of the coatings

Numerical simulation of the coating build-up with estimation of some of the coatings final characteristics was done using the commercial software Simulent-Coat (Simulent, Inc., Toronto, Canada). Simulent-Coat simulates a three-dimensional stochastic model of the thermal spray coating deposition with moving and stationary spray guns. The properties of impacting particles are calculated stochastically by probability density functions. Simulent-Coat is based on a Cartesian grid to define the computational domain and to track the shape and position of the coating surface. The model dispersed molten droplets on the substrate by generating random values of process parameters, assuming that these properties follow appropriate distributions with user-specified means and standard deviations. Splat sizes after the droplet impact were calculated from an analytical model. A set of rules has been used to describe the coalescence of splats. The porosity was assumed to be solely due to the curl-up of the splats as a result of thermal stresses. The model predicts the coating porosity, thickness and roughness as a function of the spray parameters. More details about the model can be found elsewhere [45], [46], [56], [64], [65], [250], [251], [254].

The summary of material characteristics and parameters used for the simulations of both the YSZ and alumina are shown in Table 22. Results for the simulated final coating porosity, thickness and roughness are listed in Table 23. The last two characteristics are mentioned to show how some other coating characteristics change, according to

the model, with a change in the particle size, impact velocity and temperature.

Table 22: List of material characteristics and other parameters for numerical simulations.

Parameter	Alumina	YSZ
Particle velocity	see Table 17	
Particle temperature		
Particle size (µm)	27	37 and 55
Gun loading (kg/s)	$3,5 \cdot 10^{-4}$	$6,4 \cdot 10^{-4}$
Gun velocity (m/s)	0,8	0,8
Gun distance (mm)	100	100
Viscosity (m ² /s)	$1,026 \cdot 10^{-5}$	$1,030 \cdot 10^{-5}$
Surface tension (kg/s ²)	0,69	0,5
Heat of fusion (J/kg)	$1,075 \cdot 10^6$	$0,708 \cdot 10^6$
Substrate temperature (°C)	25	25
Thermal conductivity (W/mC)	6	2
Density (kg/m ³)	3890	5600
Heat capacity (J/kgK)	1300	9628

It is evident that the absolute porosity values of that measured by the point count method and numerically simulated differ. A possible reason can be an occurrence of pullouts during a coating cross-section preparation explaining the increase in measured porosity values. Another fact is that the numerical model was found to be quite insensitive to the changes in some of the input characteristics and parameters (including the particle velocity and temperature). Still, using its assumptions and simplifications, the results of numerical simulations show qualitatively the same trend in porosity as the measured data. For all three lots of powders, the coating porosity decreased with the increase in the powder particle impact velocity and temperature. However, the simulated YSZ coating porosity increased for the powder lot of the smaller powder particle size. The model assumes all the particles to be fully molten and porosity to be the result of splat curl-up due to the thermal stresses. Better filling of the voids by smaller powder particles as well as a difference in the degree of melting of the powder particles was

omitted. The smaller particle size then means a higher number of particles necessary to fill up the simulated volume of the coating and thus more interfaces among the splats are introduced where the porosity can develop.

Table 23: Simulated coating characteristics.

Parameter set	Porosity (%)	Thickness (μm)	Roughness (μm)
Alumina powder (20-45) microns			
1	17.0	318	13.16
2	16.3	315	10.19
3	15.8	314	10.02
YSZ powder (20-45) microns			
1	15.3	317	11.75
2	14.9	314	10.86
3	14.3	312	11.82
YSZ powder (45-75) microns			
1	13.0	315	15.26
2	12.5	313	15.28
3	12.2	311	14.65

6.4 X-ray diffraction analysis of coatings

X-ray diffraction analysis of the plasma sprayed coatings was performed in order to observe the potential differences in phase compositions of coatings prepared under the different plasma spray conditions. Phase composition has substantial influence on some of the coating characteristics, such as mechanical properties, stress level and its distribution. Top surfaces of the coating samples were analysed and weight fractions of monoclinic zirconia and alpha alumina phases were calculated following the same procedure and assumptions as in 5.4.4.

Reuslts of XRD analysis performed on YSZ coatings prepared by plasma spraying under the different spray conditions and using two different lots of powders differing in

particle size ranges, that is (20 – 45) μm and (45 – 75) μm , are shown in Fig. 6.10 and Fig. 6.11. It is obvious that spectra obtained on coatings prepared from two different powders are similar. No effect of powder particle size was observed. The results of weight fraction calculations are listed in Table 24. The weight fraction of monoclinic phase dropped roughly by 30 % after plasma spraying as compared to the original powder. The same results were obtained for YSZ powders plasma sprayed into water. The differences in phase compositions among the individual coatings are negligible since the accuracy of quantitative analysis is estimated to be about 10 % [94].

XRD spectra of plasma sprayed alumina coatings are shown in Fig. 6.12. It is obvious that obtained spectra are substantially different from those obtained for alumina powder plasma sprayed into water. Besides common alumina phases in plasma sprayed coatings, such as alpha, gamma and even indications of delta and theta, existence of other peaks, marked as *c*, was observed. Two possible explanations were found for appearance of these peaks. They might originate from plasticine that has been used for sample fixation during XRD analysis. This plasticine contains very fine particles of calcium carbonate (CaCO_3), whose highest intensity peak of plane (104) is positioned at 2θ of about 29.4-29.5 and other less intensive peaks might be also found in obtained XRD patterns, mostly overlapped with alumina phases [101], [102], [103]. In [104] and [105] these peaks were assigned to newly identified alumina phase that is characterized by an orthorhombic unit cell and referred to as *U* phase. It is deemed that *U* phase is a splat boundary phase. From the reported experimental results it follows that *U* phase appears to have no crystallinity (absence of long range order) under certain conditions and

6. Plasma sprayed coatings characterization

Fig. 6.10: XRD spectra of YSZ coatings prepared from powder with size range of (20 – 45) μm plasma sprayed under different spray conditions.

Fig. 6.11: XRD spectra of YSZ coatings prepared from powder with size range of (45 – 75) μm plasma sprayed under different spray conditions.

Table 24: Weight fractions of monoclinic phase in YSZ plasma sprayed coatings.

Sample	$I_m(-111)$	$I_t(101)$	$I_m(111)$	$w_m(\%)$
Original powder	101.5	358.9	74.6	37.1
Powder particle size: (20-45) μm				
Parameter set 1 ~ 6 kW	12.2	238.3	9.0	9.6
Parameter set 2 ~ 10 kW	5.8	283.1	3.6	3.8
Parameter set 3 ~ 14 kW	6.5	286.1	7.0	5.4
Powder particle size: (45-75) μm				
Parameter set 1 ~ 6 kW	8.9	268.7	8.2	7.1
Parameter set 2 ~ 10 kW	6.6	278.0	6.8	5.5
Parameter set 3 ~ 14 kW	10.7	214.4	10.6	10.7

Fig. 6.12: XRD spectra of alumina coatings plasma sprayed under different spray conditions.

Table 25: Weight fractions of alpha phase in alumina coatings after plasma spraying.

Sample	$I_\alpha(104)$	$I_\alpha(113)$	$I_\gamma(400)$	$I_\delta(00.12)$	$w_\alpha(\%)$
Original powder	277.1	461.5	-	-	100.0
Parameter set 1 ~ 6 kW	15.6	21.5	240.6	-	14.8
Parameter set 2 ~ 10 kW	4.4	21.7	136.4	73.4	12.2
Parameter set 3 ~ 14 kW	9.0	16.0	200.2	126.7	7.9

develops into a crystalline phase due to mechanical stress induced during cutting/peeling off of the coating or thermal treatment (stress relief) of the coatings.

The weight fractions of alpha alumina phase in plasma sprayed coatings were determined using formula (17) and are listed in Table 25. Peak broadening around 2θ of 46 in XRD spectra of coatings prepared under spray parameter sets 2 and 3 can be observed. It was possible to distinguish I_γ (400) and I_δ (00.12) and to determine the respective relative intensities. Intensities of I_δ (00.12) peaks were incorporated in the weight fraction calculations. Non-symmetric I_γ (400) peak for coating prepared with parameter set 1 indicates presence of I_δ (00.12), which is not very distinct and its relative intensity could not be calculated separately. However, this does not influence the value of weight fraction. From the results obtained it is obvious that most of the original alpha phase transformed to gamma alumina phase contained in plasma sprayed coatings. The residual amount of alpha phase was found to be 8 % to 15 % that is considerably lower than for powders plasma sprayed into water. The difference is probably due to better powder melting. The alumina phase in the coatings comes from unmelted seeds of original powder particles and small amount of freshly nucleated alpha phase on these seeds. Gamma alumina phase nucleates from the molten alumina because the energy barrier to nucleation of gamma alumina is less than that of alpha alumina [106], [107].

6.5 Thermal diffusivity measurements

Thermal diffusivity is a measure of how quickly a body can change its temperature; it increases with the ability of a body to conduct the heat and it decreases with the amount

of heat needed to change the temperature of a body. In a laser flash method used in this study, the measurement of the thermal diffusivity of a material is carried out by rapidly heating one side of a sample and measuring the temperature rise on the opposite side. The time that it takes for the heat to travel through the sample and cause the temperature on the rear face to rise can be used to measure the through-plane diffusivity and calculate the thermal conductivity if the specific heat and density of the material are known.

In the plasma sprayed coatings, the thermal diffusivity value is influenced by the coating microstructure, above all the coating porosity. Since YSZ and alumina are materials transparent to impinging radiation, an energy transfer would take place by means of both the photon and phonon mechanisms, up to the critical thickness of the sample where transparency can be neglected and where energy is transferred by phonons only. Thermal diffusivity below the critical thickness is not a material constant and depends, above all, on the coating thickness and impinging radiation wavelength [157]. In order to eliminate the sample transparency and impinging radiation absorption, both sides of samples were sprayed by carbon paint prior to the measurement. The samples were disks with a standard diameter of 12.7 mm and a thickness of about 1.4 mm. Inside the laser flash apparatus, the sample disk is aligned between a laser and an IR detector. When the laser is fired, the laser beam energy strikes and is absorbed by the front surface of the sample, causing a heat pulse to travel through the sample. The resulting sample temperature rise is fairly small, ranging from about 0.5 to 2 °C.

Thermal diffusivity values measured for the YSZ and alumina coatings are listed in Table 26. The thermal diffusivities obtained are consistent with those presented in [157]

and [159]. The measurement was performed three times for each sample. The average thermal diffusivity values plotted against the parameter set number used for the sample preparation are shown in Fig. 6.13.

Table 26: Thermal diffusivity of alumina and YSZ coatings.

Parameter set	Thermal diffusivity (cm ² /s)			
	1.	2.	3.	Average
Alumina powder (20-45) microns				
1	0.01513	0.01508	0.01475	0.014987
2	0.01928	0.01945	0.01905	0.019260
3	0.01913	0.01900	0.01926	0.019130
YSZ powder (20-45) microns				
1	0.00649	0.00629	0.00611	0.006297
2	0.00530	0.00539	0.00534	0.005343
3	0.00550	0.00546	0.00534	0.005433
YSZ powder (45-75) microns				
1	0.00494	0.00497	0.00485	0.004920
2	0.00513	0.00513	0.00508	0.005113
3	0.00526	0.00527	0.00528	0.005270

From the results it can be seen that the general trend in the thermal diffusivity of the plasma sprayed YSZ and alumina coatings is to increase with increasing net energy or the powder particle impact velocity and temperature. The increase measured for the alumina coatings was more than 25 % under the different plasma spray conditions, while for YSZ powder of larger particle size the increase was only about 7 %. For the YSZ powder of smaller particle size the highest value of thermal diffusivity was obtained for coating prepared at net energy of 6 kW. This might have been caused by different amount and quality of interfaces in this coating with higher portion of unmelted material as compared to other coatings prepared from the same powder. Also, the highest amount of monoclinic phase in this coating, as indicated by XRD analysis, that has lower thermal conductivity than the tetragonal phase was suppressed by the phenomenon

6. Plasma sprayed coatings characterization

Fig. 6.13: Average thermal diffusivity vs. parameter set number.

Fig. 6.14: Thermal diffusivity as a function of measured coating porosity.

causing the increase in thermal diffusivity. Also, thermal diffusivity for the alumina coating prepared with the parameter set 3 is slightly lower than the diffusivity for the coating sprayed under the conditions of the parameter set 2. In this case, the thermal diffusivity decrease can be attributed to the splat morphology change due to the increase in the impact particle velocity. Extensive splashing of spreading particles could result in the increase in “true” porosity or could worsen the contact at the splat interfaces. This still does not collide with results of the porosity measurement where other significant phenomena took place. Thermal diffusivity of materials is not dependent only on the porosity features but also on their distribution. Material microstructure (porosity) effects the distribution of energy transferred from impinging radiation and thus the thermal diffusivity value measured. Pores and voids inside the coatings serve as obstructions for the heat transfer.

The thermal diffusivity values show an opposite dependence on the change in the plasma spray parameters than the coating porosity. A diagram of the thermal diffusivity as a function of coating porosity measured by a point count method is in Fig. 6.14. It is obvious that except the deviations described earlier, the thermal diffusivity of plasma sprayed coatings increases with decreasing porosity of the coatings. Such results agree with conclusions of other studies, e.g. [160], [240].

6.6 Electrochemical impedance spectroscopy of the plasma sprayed coatings

Electrochemical impedance spectroscopy (EIS) is an effective technique for evaluation of the plasma sprayed coating characteristics (e.g. thickness, porosity and pore

shape). Cylindrical YSZ and alumina plasma sprayed coating samples with a diameter of 12.7 mm and thickness of about 1.4 mm were used in the following EIS characterization. One side of the samples was coated by a silver paste and connected to a silver wire first and sealed by silicon after that to ensure the silver part of the sample is not exposed to the electrolyte. EIS measurements were performed over the frequency range of (10^{-2} - 10^6) Hz with applied AC potential amplitude of 5 mV and 20 mV for alumina and YSZ coatings, respectively. Obtained Nyquist and Bode plots are shown in Fig. 6.15, Fig. 6.16 and Fig. 6.17.

The EIS estimation of the plasma sprayed coatings resides in modelling the coating with a suitable equivalent AC circuit and trying to adjust its parameters so its impedance matches the measured data. In the following, the model in Fig. 6.18 was used. The proposed equivalent electrical circuit consists of the electrolyte and the plasma sprayed ceramic coating. A resistor, R_s , in series with a unit of ceramic coating, represents the solution resistance of the test electrolyte between a working electrode and a reference electrode. The ceramic coating consists of a ceramic matrix and a large number of pore inclusions. R_c in parallel with C_c is the resistance and capacitance of the thermally sprayed coating including pores. Since the pore inclusions, represented by a unit consisting of a resistor, R_p , in parallel with a capacitor, C_p , are embedded in the plasma sprayed coating, the unit is considered to be in series with a coating resistor and in parallel with a coating capacitor.

Fig. 6.15: Comparison of Nyquist and Bode plots for the alumina coatings plasma sprayed under different spray conditions.

Fig. 6.16: Comparison of Nyquist and Bode plots for the YSZ coatings, (20-45) μm , plasma sprayed under different spray conditions.

Fig. 6.17: Comparison of Nyquist and Bode plots for the YSZ coatings, (45-75) μm , plasma sprayed under different spray conditions.

Fig. 6.18: Equivalent AC circuit employed for the EIS data evaluation.

The first plateau in Bode diagrams can be related to the coating resistance R_c . The value of the equivalent coating resistance was obtained by three different ways: 1) fitting the proposed model parameters so the model impedance matches the experimental data, 2) extrapolation of the semicircles in Nyquist plot, and 3) extrapolation of the plateau in impedance vs. frequency Bode plot. When fitting the model to the experimental data, constant phase elements in the place of ideal capacitors were used, because coating uneven surfaces give rise to the frequency dispersion and the non-uniform distribution in the current density. The average value of all three estimates was taken as the electrical resistance of the plasma sprayed coating. It can be assumed that the coating resistance is, according to the Ohm's law, linearly proportional to its thickness:

$$R_c = \rho_c \frac{D_c}{A} \quad (18)$$

where ρ_c is the coating resistivity, D_c is the coating thickness and A is the area exposed to electrolyte. Since the sample area is the known constant (diameter of 12.7 mm) and

the sample thickness was measured for each sample prior to applying the silver coating and silicone sealing, the electrical resistivity could be calculated by multiplication coating resistance by its area and normalizing the value to the unity of coating thickness. The calculated values of electrical resistivity for all the samples are listed in Table 27. From the results it can be seen that with the increase in spray net energy the plasma sprayed coating electrical resistivity increased significantly for all three types of coatings.

The electrochemical impedance response for a material depends on microstructural features such as pores and defects through which conductive electrolyte can penetrate. It was shown by previous observations of the YSZ and alumina plasma sprayed coatings that with increasing spraying net energy, coating porosity decreased while the cohesion improved. With such defects reduced in the coating, less electrolyte, which ensures the electrical conductivity in the EIS measurement, can penetrate through the coating and electrical resistivity (resistance) increases. The electrical resistivities of the YSZ and alumina ceramics at the room temperature were estimated to be 1.41×10^{11} and about $10^{14} \Omega \cdot \text{cm}$, respectively. Thus, the YSZ and alumina coatings, several hundred microns thick, should account for electrical resistances of about 10^{10} and $10^{13} \Omega$, respectively. However, the measured values are much smaller. This can be attributed to the aqueous conductive electrolyte that can penetrate in the coatings, thereby decreasing the ceramic resistance. The resistivity of the electrolyte used in this study was measured to be $9.5 \Omega \cdot \text{cm}$ [235], which gives the resistance of electrolyte, in the same thickness and cross-sectional area as coating samples, to be several Ohms. This is several orders of magnitude lower than the measured values for the coating samples.

Table 27: Calculated coating electrical resistivity and pore resistance for all ceramic coatings.

Parameter set	Coating electrical resistivity, ρ_c ($\Omega\cdot\text{cm}$)	Pore electrical resistance, R_p (Ω)
Alumina powder (20-45) microns		
1	15547.21	5999.13
2	37448.40	23702.37
3	128997.27	25702.60
YSZ powder (20-45) microns		
1	13633.74	15262.72
2	43046.83	56225.71
3	46100.27	69160.88
YSZ powder (45-75) microns		
1	9390.79	5725.85
2	18568.87	16697.70
3	21330.90	17905.32

The relative value of R_c depends on the so-called effective resistivity of the plasma sprayed coating whose pores are filled with conductive electrolyte during the EIS measurement. The effective resistivity of the coating with open pores can be expressed according to the rule of mixture for composite materials:

$$\rho^{eff} = \rho_c V_c + \rho_e V_e \tag{19}$$

where ρ_c and ρ_e are the resistivities of YSZ and electrolyte, respectively. The V_c and V_e refer to the volume fractions of the YSZ and electrolyte that fills the open pores. The increase of R_c is due to the lower porosity and contributes to the higher effective resistivity with an increase in the volume fraction of the coating. The effective resistivity of a cracked specimen should decrease since the volume fraction of electrolyte with lower resistivity increases, and R_c should decrease as well [234].

Fig. 6.19: Calculated electrical resistivity vs. measured coating porosity.

Obviously, the electrical resistivity of the coating depends on the porosity and the pore shape. The calculated electrical resistivity of the coatings and estimated values of porosity by a point count method are shown in Fig. 6.19. For the YSZ coatings the resistivity shows almost linear dependance on the porosity. For the alumina coatings there is a significant increase in the coating resistivity for the coating prepared at the highest net energy value.

In the second column in Table 27, there are calculated values of pore electrical resistances, R_p , for all the YSZ and alumina coatings. The pore resistance of the coatings increases with the increase in spray net energy which correlates with the increasing ceramic coating resistivity. The correlation dwells in a proposed pore shape change [235]. The pore resistance, or the transmission resistance at the double layer between ceramic and electrolyte in the pore inclusion, can be expressed, according to the Ohm's law, as:

$$R_p = \rho_p \frac{D_p}{A_p} \quad (20)$$

where ρ_p is the resistivity of the double layer between ceramic and electrolyte in the pores, D_p is the double layer thickness in which an electrochemical reaction occurs and that can be assumed to be a constant, and A_p is the cross-sectional area of the double layer. Therefore, pores of small sizes (small values of A_p) correspond to the large pore resistance values and vice versa. Therefore, it can be concluded that the increase of net energy used for preparation of the plasma sprayed coatings resulted in the decrease in porosity. It was suggested that due to the higher velocities and temperatures of impacting particles such coatings have a higher contact area between the splats and thus better cohesion. This leads to the decrease in lateral discontinuities and can lead to the more extensive vertical cracking of the individual splats due to the higher spreading factor. Influence of the crack direction on the pore resistivity is obvious from an equation (20). It is expected that longitudinal cracks correspond to very small values of the pore resistance as their cross-sectional area is very large. For vertical cracks in the coating, their corresponding resistance is much higher, as the pore cross-sectional area is smaller.

Several properties, related to coating microstructure, of plasma sprayed YSZ and alumina coatings were investigated. SEM analysis revealed that in spite of the particles impact on the hot previously deposited layers there are still differences in splat morphology and thus in coating microstructure. The coating porosity decreased by a factor of about 2 and 1.6 with increasing particle velocity and melt fraction for YSZ and

alumina coatings, respectively. Phase compositions changes, evaluated by XRD analysis, were characterized by 30 % drop in monoclinic zirconia phase and only 15 % of the remaining alpha alumina phase in coatings. With higher spray net energy higher thermal diffusivities were measured indicating changes in the coating microstructure in terms of lower porosity and improved intersplat contacts. The porosity and quality of interfaces were also evaluated by an electrochemical impedance spectroscopy. With the change in spray conditions, towards higher powder melting and velocities, the coating electrical resistivity and pore resistance increased significantly. Obtained results were in agreement with previous measurements and were explained by the decrease in coating porosity and change in the pore size and shape.

7. CONCLUSIONS

The plasma spray is a versatile technology that has been found successful as a reliable and cost effective method for depositing functional coatings on the surface of engineering components. Due to the ever-increasing field of applications as well as the widening range of properties demanded of plasma sprayed coatings, a deeper understanding of this complex process and its controlling parameters has become essential. In the present study, influences of several process parameters on the plasma spray deposits were investigated following sophisticated experimental design. The whole plasma deposition process was divided into three subsequent parts examining the effect of different spray conditions in terms of changing plasma spray parameters on: 1) the powder particle in-flight velocity and temperature, 2) the splat formation and particle degree of melting, and 3) the final coating properties.

1) It was concluded that the particle in-flight characteristics can be significantly changed by a selection of the spray parameters. Dominant influences of three spray parameters were observed. It was found that the particle velocity and temperature increased roughly by 45 % (from 110 to 160 m/s) and 14 % (from 2150 to 2450 °C), respectively, due to the increase of 10 kW in the net energy. Quantitatively similar effects were observed when the spray distance was changed, however, observed characteristics increased with decrease in the spray distance from 250 to 100 mm. Higher flow rate of the main gas led to the significant increase in the particle velocity (23 %) and rather moderate decrease in the particle temperature (3.5 %). Increase in the auxiliary gas flow

rate up to 10 wt.% in the Ar+He gas mixture resulted in increase of the particle in-flight velocity, while the particle temperature decreased. Existence of the optimal value of the carrier gas flow rate, at which the powder particles attain maximum velocity and temperature, was indicated. No influence of the powder feed rate, being below 30 % of the plasma gas mass flow rate, on the particle velocity and temperature was observed.

2) Three different sets of plasma spray parameters were used for the deposition of YSZ and Al_2O_3 splats on the surface of mirror-polished stainless steel substrates at room temperature. In case of YSZ splats, impacting particles had temperatures below the material melting point and deposition efficiency was very low. All the splats show some degree of splashing. With the increasing particle velocity and temperature (higher temperatures were achieved for fine powder) splashing was higher and the observed splats thinner. Spreading of the particles was controlled by the localized solidification and bonding of the particle material to the substrates. The alumina particle temperatures were above the material melting point. Disk-shaped alumina splats deposited under the low velocity and temperature conditions showed good conformity and adherence with the substrate. Disk-shaped splats changed into highly splashed ones with the increasing particle velocity.

Better powder melting was observed by SEM for powders plasma sprayed at higher net energy. Melt fraction of YSZ powder increased more than 2 times and decreased with the increasing particle size. Raman spectroscopy and X-ray diffraction revealed higher content of tetragonal zirconia and gamma alumina phases after spraying at higher net energy. Semi-quantitative XRD analysis showed drop by more than 30 % in weight

fractions of the original zirconia and alumina phases due to the formation of metastable ones indicating better powder melting.

3) SEM observations of top surfaces of YSZ and alumina coatings confirmed existence of different splat morphologies as a result of different spray conditions. The differences were found to be in agreement with the observations of single splats and evaluation of the degree of particle melting. XRD analysis performed on zirconia and alumina coatings revealed drop in zirconia monoclinic phase by 30 % and only residue of 15 % of the alpha alumina phase in the coatings.

The porosity of alumina coatings estimated by a point count method decreased from 23 % to 14 % with increase in the spray net energy. For YSZ coatings the porosity values were generally higher, decreasing with the powder particle size, but still showing the significant decreasing trend with the lowest porosity values slightly above 20 %. Decreasing trend of coating porosity was also assessed by numerical simulation.

The thermal diffusivity of the plasma sprayed coatings, in principle, increased with the increase in spray net energy. For the YSZ coatings measured values changed from about 0.0049 to 0.0054 cm²/s (~ 10 %) and were higher for the coatings prepared from finer YSZ powder. The thermal diffusivity of alumina coatings increased by 28 %. The results of thermal diffusivity measurements were linked to the porosity of the coatings.

The ceramic coating electrical resistivity and the pore resistance were evaluated by electrochemical impedance spectroscopy. Increase in both characteristics with the increase in plasma spray net energy was explained by the quality of interfaces in the

coating, the decrease in the coating porosity and the change in the pore size and shape.

The significant influence of several input plasma spray parameters on the final coating properties was manifested. The effect of such parameters on different stages of the plasma spray deposition process was studied and proved by various experimental and analytical techniques. It was demonstrated that by a proper parameter selection, the powder particle in-flight characteristics could be controlled resulting in the different splat morphologies. The powder particle impact velocity and temperature thus affect the coating microstructure that, to a large extent, determines the coating properties. It is believed that further research together with the development of diagnostic techniques and modelling will bring new and improved insights that will help to enhance the understanding of the plasma spray process as well as improve the process repeatability and reproducibility, which are of high importance and great practical interest.

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APPENDIX 1: LIST OF PUBLICATIONS

Papers published in scientific journals:

PROCHAZKA, Z., KHOR, K.A., CIZEK, J. *Influence of Input Parameters on Splat Formation and Coating Thermal Diffusivity in Plasma Spraying*. Advanced Engineering Materials, Vol. 8, Issue 7, 2006, pp. 645-650.

CIZEK, J., KHOR, K.A., PROCHAZKA, Z. *Influence of Spraying Conditions on Thermal and Velocity Properties of Plasma Sprayed Hydroxyapatite*. Materials Science and Engineering: C, Vol. 27, 2007, pp. 340-344.

Forthcoming:

PROCHAZKA, Z., KHOR, K.A. *On the Influence of Plasma Spray Parameters on In-flight YSZ Particles Velocity and Temperature*.

PROCHAZKA, Z., KHOR, K.A. *Alumina and Zirconia Splat Formation under the Different Plasma Spray Conditions*.

Conference papers:

PROCHAZKA, Z., KHOR, K.A., CIZEK, J. *Influence of Input Parameters on Splat Formation and Coating Thermal Diffusivity In Plasma Spraying*. 3rd International Conference on Materials for Advanced Technologies, Singapore 2005.

CIZEK, J., KHOR, K.A., PROCHAZKA, Z. *Influence of Spraying Conditions on Thermal and Velocity Properties of Plasma Sprayed Hydroxyapatite*. 3rd International Conference on Materials for Advanced Technologies, Singapore 2005.

PROCHAZKA, Z., KHOR, K.A., CIZEK, J. *Impact of Input Parameters on Thermal Diffusivity of Plasma Sprayed Coatings*. European Congress on Advanced Materials and Processes EUROMAT, Prague, Czech Republic 2005.

CIZEK, J., PROCHAZKA, Z., KHOR, K.A. *Bone Replacement Materials Development: Temperature and Velocity Characteristics of Plasma Sprayed Hydroxyapatite Powder*. European Congress on Advanced Materials and Processes EUROMAT, Prague, Czech Republic 2005.

PROCHAZKA, Z., KHOR, K.A. *Study on Splat Formation in Alumina and Zirconia Powders Sprayed under Different Plasma Spray Conditions*. Asian Thermal Spray Conference ATSC, Nagoya, Japan 2005.

APPENDIX 2: LIST OF FIGURES

Fig. 1.1: Scheme of different stages in the plasma spray process.....	13
Fig. 1.2: Scheme flowchart of experimental investigations.....	16
Fig. 2.1: Typical coating cross section illustrating lamellar structure [3].	19
Fig. 2.2: Current and potential thermal spray coating applications for aircraft turbine engine parts [9].	20
Fig. 2.3: Sketch of wires/rods flame spray technique [3].	24
Fig. 2.4: Sketch of high-velocity oxy-fuel spray torch [13].	24
Fig. 2.5: Detonation gun spray system [13].	25
Fig. 2.6: Sketch of an arc spray gun [3].	26
Fig. 2.7: Sectional view of a plasma torch with gas-stabilized arc [3].	28
Fig. 2.8: Schematic of plasma gun with water-stabilized arc [12].	29
Fig. 2.9: Schematic of inductively coupled plasma torch.	30
Fig. 2.10: Plasma jet generation [16].	32
Fig. 2.11: Main regions of a transient plasma jet [18].	34
Fig. 2.12: Effect of a carrier gas flow rate on particle penetration into the plasma jet.....	38
Fig. 2.13: Velocity distributions of sprayed particles as a function of ambient pressure at different spray distances. The particle velocities increase as the pressure drops and the rapid increase of particle velocity is observed at below 150 torr (modified from [83]).	42
Fig. 2.14: In-flight velocity and temperature of nickel particles measured at various spray distances (modified from [50]).	44
Fig. 2.15: Plots illustrating effects of gun current, H_2 , total gas and carrier gas flow rates and axial spray distance on the average temperature and velocity of partially stabilized zirconia particles; values are normalized in respect to highest value measured (modified from [78]).	45
Fig. 2.16: Two different alumina splat morphologies: disk-shaped and splashed splat (diameter of about 50 μm).	49

Fig. 2.17: Illustrations of selected splat characteristics [54].	51
Fig. 2.18: Pictures representing evolution of the cooling rate and flattening degree with the particle velocity, size and temperature, respectively, for zirconia particles sprayed onto 304L stainless steel mirror-polished ($R_a < 0.1\mu\text{m}$) substrates at 75 and 300°C (below and above the transition temperature) [52].	54
Fig. 2.19: Calculated temperature at the interface of substrate-splat and at the surface of splat during its deposition (PSZ droplet with 400 K overheating on steel substrate). The interface temperature rise from ambient to over 2000 K in less than $1\mu\text{s}$ leads to a heating rate in the order of 10^9 K/s. This extremely fast temperature rise will explosively evaporate and expand the adsorbed gas/condensates [68].	60
Fig. 2.20: Droplet spreading on the substrate with and without condensates/adsorbates [68].	61
Fig. 2.21: Schematic of temperature gradients vs. interface velocity showing regions of different solidification microstructure [61].	62
Fig. 2.22: Two different morphologies revealed in splat after solidification [3].	65
Fig. 2.23: Generation of a thermal residual stress in a ceramic coating deposited on a metallic substrate (coefficient of thermal expansion of a ceramic coating is lower than that of a substrate).	71
Fig. 2.24: Three polymorphs of zirconia [205].	73
Fig. 2.25: Transformation zone around crack tip [88].	75
Fig. 2.26: Fracture toughness versus composition for transformation toughened ZrO_2 -based materials [88].	76
Fig. 2.27: Phase diagram of the ZrO_2 -rich region of the ZrO_2 - Y_2O_3 system. M – monoclinic phase, C – cubic phase, T – tetragonal phase, L – liquid, t' – nontransformable tetragonal phase [108].	78
Fig. 2.28: Schematic picture of the hexagonal close packed structure and α -alumina crystal structure.	80
Fig. 2.29: Equilibrium diagram for the system Al - Al_2O_3 [124].	82
Fig. 3.1: SEM pictures of as-received YSZ powder particles: surface and cross-section.	89
Fig. 3.2: Particle size distributions for original YSZ powder and powders after sieving to	

different size ranges.	90
Fig. 3.3: SEM pictures of as-received alumina powder particles: surface and cross-section.	92
Fig. 3.4: Particle size distributions and respective cumulative functions of as-recieved and sieved alumina powders.	92
Fig. 3.5: Sectional view of SG-100 plasma spray torch with a radial powder feeding [146].	96
Fig. 3.6: SprayWatch camera to the plasma spray jet and the sample holder adjustment.	98
Fig. 3.7: Schematic of the holder used for a single splat deposition.	98
Fig. 3.8: SprayWatch thermal spray monitor consists of a camera unit with spectrally resolving optics and an industrial PC [147].	99
Fig. 3.9: Measurement principle of the average particle temperature in the SprayWatch system [147].	101
Fig. 3.10: Temperature rise with time.	103
Fig. 3.11: Nyquist plot with impedance vector.	106
Fig. 3.12: Bode plot with one time constant.	107
Fig. 4.1: Example of an average temperature record, with the standard deviation for individual measurements, influenced by unsteady powder feeding.	112
Fig. 4.2: Change of the particle velocity time dependance with net energy.	114
Fig. 4.3: Change of the particle temperature time dependance with net energy.	114
Fig. 4.4: Dependance of the average particle velocity and temperature on a step change of various parameters, such as net energy; main, auxiliary and carrier gas flow rates, powder feed rate and spray distance. Vertical bars represent standard deviations.	116
Fig. 4.5: Critical combinations of the particle velocity and temperature.	121
Fig. 4.6: Temperature versus velocity of in-flight particles sprayed under conditions listed in Table 11.	123
Fig. 4.7: Change of average values of the particle velocity with a change in the level of given parametr.	129
Fig. 4.8: Change of average values of the particle temperature with a change in the level of given parametr.	129

Fig. 4.9: Average velocity and its parameter function in respect to a run order.....	132
Fig. 4.10: Average temperature and its parameter function in respect to a run order. ...	132
Fig. 5.1: SEM pictures of YSZ (45-75) μm deposited with the parameter set 1 (a-b), 2 (c-d) and 3 (e-f).	137
Fig. 5.2: SEM pictures of YSZ (20-45) μm deposited with the parameter set 1 and spray distance of 50 mm (a), 1 with spray distance of 150 mm (b), 2 (c-d) and 3 (e-f)...	140
Fig. 5.3: SEM pictures of alumina (20-45) μm deposited with parameter set 1 using 4 kW (a), parameter set 1 (b), 2 (c-d) and 3 (e-f).	142
Fig. 5.4: Selected features. Optical micrographs - area under the shielding plate orifice: (a) YSZ, (b) alumina; substrates after splat rebounding (c-d). SEM - YSZ rebounded particles (e), YSZ splat spreading (f).....	146
Fig. 5.5: Surface and cross-section SEM pictures of YSZ powder plasma sprayed into water, particle size (45-75) μm : parameter set 1 (a-b), 2 (c-d) and 3 (e-f).....	151
Fig. 5.6: Powder particle <i>MFP</i> as a function of the particle diameter for YSZ powders prepared under different spray conditions.	154
Fig. 5.7: Surface and cross-section SEM pictures of alumina powder plasma sprayed into water: parameter set 1 (a-b), 2 (c-d) and 3 (e-f).....	157
Fig. 5.8: Raman spectra of the starting powder (4.5 mol. % of yttria) and powders containing 0, 3 and 10 mol. % of yttria.....	161
Fig. 5.9: Raman spectra of the starting YSZ powder, un-melted and melted particle after the plasma spraying (c, t, m indicate cubic, tetragonal and monoclinic phases respectively).....	162
Fig. 5.10: Raman spectra of the original alpha alumina particles, partially and fully melted particles after the plasma spraying.....	164
Fig. 5.11: XRD spectra of YSZ powders sprayed into water under different spray conditions.....	167
Fig. 5.12: XRD spectra of the alumina powders sprayed into water under different spray conditions.....	169
Fig. 6.1: SEM pictures of the top and fractured surfaces of YSZ coatings prepared by deposition of powder with the particle size range of (45 – 75) μm : parameter set 1	

(a-b), 2 (c-d) and 3 (e-f).....	175
Fig. 6.2: SEM pictures of the top and fractured surfaces of YSZ coatings prepared by deposition of powder with the particle size range of (20 – 45) μm : parameter set 1 (a-b), 2 (c-d) and 3 (e-f).....	176
Fig. 6.3: SEM pictures of the top and fractured surfaces of alumina coatings: parameter set 1 (a-b), 2 (c-d) and 3 (e-f).....	178
Fig. 6.4: Scheme of different defects denominated as porosity.....	179
Fig. 6.5: Image acquire design for the porosity determination.....	182
Fig. 6.6: Average porosity measured by a point count method.	184
Fig. 6.7: Change in the alumina coatings porosity with thickness.	184
Fig. 6.8: Change in the YSZ (20 – 45) μm coatings porosity with thickness.....	185
Fig. 6.9: Change in the YSZ (45 – 75) μm coatings porosity with thickness.....	185
Fig. 6.10: XRD spectra of YSZ coatings prepared from powder with size range of (20 – 45) μm plasma sprayed under different spray conditions.....	190
Fig. 6.11: XRD spectra of YSZ coatings prepared from powder with size range of (45 – 75) μm plasma sprayed under different spray conditions.....	190
Fig. 6.12: XRD spectra of alumina coatings plasma sprayed under different spray conditions.....	191
Fig. 6.13: Average thermal diffusivity vs. parameter set number.	195
Fig. 6.14: Thermal diffusivity as a function of measured coating porosity.....	195
Fig. 6.15: Comparison of Nyquist and Bode plots for the alumina coatings plasma sprayed under different spray conditions.....	198
Fig. 6.16: Comparison of Nyquist and Bode plots for the YSZ coatings, (20-45) μm , plasma sprayed under different spray conditions.	199
Fig. 6.17: Comparison of Nyquist and Bode plots for the YSZ coatings, (45-75) μm , plasma sprayed under different spray conditions.	200
Fig. 6.18: Equivalent AC circuit employed for the EIS data evaluation.	201
Fig. 6.19: Calculated electrical resistivity vs. measured coating porosity.....	204

APPENDIX 3: LIST OF TABLES

Table 1: Thermal spray coating properties of importance for various applications [8]. .. 21

Table 2: Comparison of thermal spray processes [4], [10], [11]. 23

Table 3: Lattice parameters of three zirconia polymorphs. 73

Table 4: Selected properties of ZrO₂ and Al₂O₃ ceramics..... 77

Table 5: Lattice parameters of hexagonal and cubic alumina polymorphs. 80

Table 6: Typical chemical composition of AISI 316L stainless steel [145]..... 94

Table 7: Compiled sets of plasma spray parameters..... 97

Table 8: Main specifications of SprayWatch measuring system [148]. 100

Table 9: Fixed set of spray parameters and parameter variation ranges..... 113

Table 10: Average particle velocity and temperature evolution with a step change in input
spray parameters. 117

Table 11: Ten sets of spray parameters used for YSZ splats preparation..... 122

Table 12: Taguchi design of experiment with results of average velocity and temperature.
..... 127

Table 13: Tabulated values of *F* test with 2 and 23 degrees of freedom..... 127

Table 14: Results of ANOVA analysis for the particle velocity. 127

Table 15: Results of ANOVA analysis for the particle temperature. 128

Table 16: Indices of parameter levels and summarized parameter functions..... 133

Table 17: Velocity and temperature of particles for splat deposition (see Table 7 for spray
parameters 1-3). 136

Table 18: Average ‘melt fraction in particle’ (*MFP*) and ‘melt fraction’ (*MF*) for YSZ
powders plasma sprayed at different conditions..... 154

Table 19: Weight fractions of monoclinic phase in YSZ powders after plasma spraying.
..... 167

Table 20: Weight fractions of alpha phase in alumina powders after plasma spraying. 169

Table 21: Average porosity of the coatings determined by a point count method. 183

Table 22: List of material characteristics and other parameters for numerical simulations.
..... 187

Table 23: Simulated coating characteristics.	188
Table 24: Weight fractions of monoclinic phase in YSZ plasma sprayed coatings.	191
Table 25: Weight fractions of alpha phase in alumina coatings after plasma spraying..	191
Table 26: Thermal diffusivity of alumina and YSZ coatings.	194
Table 27: Calculated coating electrical resistivity and pore resistance for all ceramic coatings.	203