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List of Abbreviations

AB	AcidBrite etched
AFM	Atomic force microscope
Alm 29	P3 Almeco 29 etched
В	Boehmitised
BE	Binding energy
BT	Boehmitised and thermally treated
BWI	Boehmitised
CCD	Charge-coupled device
DG	Polished and degreased
F	Etched (with AcidBrite)
EDS	Energy dispersive spectroscopy
FRDA	Elastic recoil detection analysis
FT	Etched and thermally treated
FPI	Forest Products Laboratory
FPI	FPL etched
FTIR	Fourier transform infra-red
	Fourier transform infra-red - reflection absorption spectroscopy
FW/HM	Full width half maximum
	High velocity air fuel
	High velocity an iden
K	Sommerfeld flattening criterion
KE	Kinetic energy
K.	Modified Sommerfeld flattening criterion
	Modium donsity polyothylono
Г D2	P2 atched
	P2 elulary other other kotone)
	Poly(ally) ether ether kelone)
	Poly(entrylene telephilialate)
	Poly(nemy memoryate)
DT	Poly(pitenyletie sulpitue) Polished and thermally treated
	Point of zero charge
P20	Measure of surface roughness
DRQ	Putherford backscattering
	Revine route backscallening
SEM	Scanning electron microscope
	Skewness
	Standard litres per minute
	Class transition temperature
т	
ν _t	Meher number
YANES	Y-ray absorption near-edge studies
YPS	X-ray absorption hear-eage studies
	Ariay photoelection spectroscopy
ξm	Madejski flattening ratio



1 Introduction

The processing industry increasingly requires materials which are resistant to highly erosive and corrosive environments. Whilst there are some materials that possess the required properties to be stable in these environments they are often prohibitively expensive to employ or difficult to form. One method to circumvent these issues is to form the bulk of a part from a cheap material such as aluminium or steel and then coat with a material that will withstand the harsh processing conditions. One such technique is thermal spray coating.

Thermal spray is a term that covers a variety of techniques which all operate on the same basic principle, a powder or wire is coated onto a substrate by heating and accelerating it onto the substrate. The coating is built up as a series of pancake-like splats where each powder particle or droplet has impacted and spread across the substrate or a previously deposited layer of splats. Thermal spray is not a new technique, it has in fact been in use since the early 20th century when a wire-arc device and a flame spray device were invented. In the early days thermal spray was used as a method to replace worn material on axles and bearings. Thermal spray has, however, come a long way since and the different techniques available make it possible to spray a wide variety of materials from polymers to ceramics including metals, intermetallics and cermets.

This research is primarily focussed on the use of high velocity air fuel (HVAF) and plasma thermal spray to coat aluminium with a polymer coating resistant to the corrosive environments in a food processing plant. The polymer of interest is poly(aryl ether ether ketone) (PEEK) and the substrate of interest is aluminium. The research focussed on the interaction of single splats with the aluminium substrate as complete understanding of the interactions taking place on the level of single splats is a crucial step to understanding the wider area of adhesion, corrosion and wear resistance.

The polymer PEEK was of interest due to its physical and material properties. PEEK has a high resistance to acid and alkali attack, and possesses good thermal stability and a high toughness (in terms of polymers). These properties make PEEK suitable for use in the food processing industry where the clean-in-place processes use high temperature alkali solution as part of the cleaning cycle. These same properties make it suitable as a matrix material in the formation of abradable coatings for the aerospace industry. Aluminium was selected as the substrate of choice for two reasons. Firstly aluminium is currently unable to be used in contact with food products in the food processing industry due to regulatory constraints. The use of a suitable coating would, however, open up the use of aluminium in the food processing industry. Aluminium is conversely used to a great extent in the aerospace industry, but there are situations where a wear resistant or abradable coating are required, and it is believed that PEEK may be able to form such a coating. Secondly, to achieve an investigation into the effect of surface chemistry on splat interactions with a surface, a material with a readily altered surface chemistry was required. Aluminium is good for this reason as there has been a large body of research into the surface properties of aluminium and how to alter them.

HVAF is a continuous combustion spray technique. Compressed air and kerosene are fed into a combustion chamber at high pressure and high flow rate. The combustion products expand at supersonic velocities and are directed down a straight nozzle. The powder is fed into the nozzle entrance and is entrained in the gas jet. The powder particles are then heated and accelerated by the gas jet until they impact the substrate. HVAF has been a field of thermal spray that has been overlooked in the most part by researchers with very little published on the process. The HVAF technique has generally been overlooked as the HVOF technique has a greater flexibility to be employed on a wider range of powder stock. The deposition efficiency of HVAF systems is low in comparison to HVOF systems. The combination of these fiscal disincentives has resulted in low industrial and academic uptake of HVAF systems. However, it is thought that the high velocity of the technique, and the lower temperature and less oxidising environment than is the case with HVOF (high velocity oxygen fuel) will make HVAF a suitable technique for the spraying of polymer coatings.

In contrast to HVAF, plasma is an industry standard for thermal spray. Particles are carried on a high pressure gas stream and fed through a plasma generated between a fixed anode and cathode. Plasma spray typically achieves temperatures between 1800°C and 2400°C compared to approximately 1200°C for HVAF systems. Similarly velocities achieved by the two systems differ significantly, with typical plasma particle velocities of 200 ms⁻¹ to 400 ms⁻¹ compared to particle velocities of 500 ms⁻¹ to 650 ms⁻¹ in HVAF systems.

Polymers have been subject to little investigation in the thermal spray industry. This is due to a narrow operating window which is unique to each polymer. The operating window is primarily dictated by the temperature the particles must reach in order to spread and flow upon impact, and by the temperature at which the polymer will start to undergo thermal degradation. The operating conditions are further complicated by the low thermal conductivity of polymers which results in high thermal gradients through a particle and corresponding differences in material properties. Finally polymers tend to wet metals poorly which results in coatings with insufficient adhesion.

Currently the predominant theory about thermally sprayed polymer coatings is that their adhesion to the substrate is simply due to mechanical interlocking. However, chemical bonding has been shown to be an important bonding mechanism in other coating systems (packaging, adhesive bonding) and therefore is probably an important factor in thermal spray coating adhesion also. To investigate this different chemical etchants that modify the surface chemistry of aluminium were applied to the substrates, the surface chemistry of the substrates analysed, and the interaction of PEEK with the different surface chemistries was evaluated.

This work will be presented as follows. Firstly the published work concerning aluminium surface chemistry, thermal spray of polymers and thermal spray single splats is reviewed. Then the methodology and results pertaining to the surface chemistry of the selected aluminium pretreatments will be presented. After the effects of pretreatments have been discussed, the methodology of single splat collection and image analysis of the splats is presented. The thermal spray results will be presented in two sections, plasma results and HVAF results, which will each comprise of two subsections, the effects of substrate surface chemistry and morphology, and of substrate temperature on single splat morphology. Each results section concludes with summary discussion placing the findings in the holistic picture of thermal spray research, with the conclusions reached presented at the end.

2 Literature Review

2.1 Surface chemistry and morphology of aluminium

Aluminium is a highly reactive metal, yet it has found many practical uses in everyday life due to its oxide layer that is ubiquitous with the metal. The oxide layer on aluminium is dense, well bonded to the metal, provides a physical barrier to oxygen, preventing corrosion, and is stable between pH 3-9 [1]. Surface chemistry and surface morphology of an aluminium substrate are both expected to have a significant effect on the adhesion of a coating [2-17]. Surface chemistry will affect the wetting of the coating on the substrate, and the bonding of the coating to the substrate. The surface morphology will affect the surface area available for bonding between substrate and the coating, and will affect the degree of mechanical interlocking between substrate and coating.

The surface chemistry of the oxide layer can be varied by a number of different techniques including boehmitising (the formation of a layer of boehmite on the surface of the aluminium by immersion in water at 100°C), acid etching and thermal treatment amongst others, used separately or in combination with each other [1, 3, 5, 7-9, 18-21]. This research focussed on degreased, degreased and thermally oxidised, acid etched, acid etched and thermally oxidised, boehmitised, and boehmitised and thermally oxidised aluminium surfaces.

The native oxide layer formed on aluminium surfaces is typically 2-5nm thick and composed of a series of layers. Water reacts with this native oxide to form aluminium trihydroxides, aluminium oxy-hydroxides and chemically and physically adsorbed hydroxides [1, 22]. The first layer above the parent metal is an amorphous layer of γ -Al₂O₃, subsequent layers above this have increasing levels of hydration [22]. The subsequent layers that form under ambient conditions are typically the gel-like pseudo boehmite, crystalline boehmite, both structural variations of aluminium oxide hydroxide (AlOOH), and/or bayerite, or gibbsite, both structural variations of aluminium trihydroxides (Al(OH)₃). A schematic of the native oxide layer of aluminium is presented in Figure 2.1.



Figure 2.1 Schematic of the oxide layer on aluminium reproduced from [1].

Fourier-transform infra red (FTIR) spectroscopy has been widely used to investigate the bonding and co-ordination of hydroxide ions on the surface of aluminium oxide [23-25]. Tsyganenko and Mardilovich have proposed a mechanism for aluminium oxide hydration by hydroxide ions that comprehensively explains the results gathered through FTIR analysis of hydrated aluminium oxide [24]. This work relates to the hydration hydroxylation layer as shown in Figure 2.1. Hydroxide ions bound to the alumina structure can be separated into three categories, according to the number of metal atoms they are bound to. Thus we have type I, II, and III hydroxide ions, bound to one, two or three aluminium atoms in the crystal structure. The aluminium atoms in the oxide layer can be either octahedrally (AI^{VI}) or tetrahedrally (AI^{VV}) co-ordinated. This results in six possible hydroxide bonding positions, as illustrated in Figure 2.2 [24]. This is only one potential form of a hydrated aluminium oxide layer, but it illustrates the many variables present. Not only will different surfaces have differing degrees of hydration and different ratios of oxygen, hydroxide and aluminium ions, but these ions can also be in different structural configurations with different bonding energies associated with these different positions. This means that the aluminium surface that adhesion will occur at is certainly going to be an aluminium oxide, and likely to be hydrated in one form or another by atmospheric moisture. The exact state of the surface of aluminium alloys is further complicated by hydrogen bonding between chemisorbed water, hydroxide and oxide ions. Thermal energy results in the dehydration of the oxide layer, but the paths are not straightforward and there are many intermediate hydrated forms of aluminium oxide before corundum (α -aluminium oxide) is formed, as shown in Figure 2.3.



Figure 2.2 Left, bonding schemes for hydroxide ions on an alumina surface [24]. Right, chemisorbed water structures [22].



Figure 2.3 The transformation sequence of Al(OH)₃ to Al₂O₃ reproduced from [22].

Thermal dehydration of aluminium oxide will result in different oxides on the surface depending on the ambient conditions during heating, the temperature it is heated to, and the time the surface is held at the given temperature, as governed by the phase diagram for the aluminium-water-air system [18]. This work relates to the oxide layer as shown in Figure 2.1. Thermal treatment of an acid etched surface results in the progressive removal of hydroxide ions from the oxide layer until eventually corundum is formed. The dense anhydrous layer formed during acid etching however restricts the thickness of the oxide layer to that formed in the etching process [8].



Figure 2.4 The Aluminium oxide – water equilibrium phase diagram, reproduced from [22].

Acid etching of aluminium surfaces dissolves the native oxide present on the surface and forms a new oxide layer. The properties of the new oxide layer are dependent on the chemical composition of the etchant. It is important to note that not only do acid etches modify the surface chemistry of the aluminium but also the surface morphology, again with different etchants resulting in different morphology. Acid etches typically result in a dense anhydrous oxide layer with a thin top layer of hydrated oxides such as pseudo-boehmite, gibbsite and/or bayerite [1, 8]. The exact morphological properties of the surface vary from etchant to etchant, but typically a shallow open porous structure is formed that increases bonding area and provides for mechanical keying with a coating [1].

For many years the forest products laboratory (FPL) etchant was the pretreatment of choice for the formation of adhesively bonded aluminium joints in aircraft. The FPL etchant (a combination of sodium dichromate and concentrated sulphuric acid, details in Table 3.2) produced a scalloped surface with whiskers enabling good mechanical interlocking with adhesives [4, 8, 9, 26]. Phosphoric acid anodising and sulphuric acid anodising are also used as pretreatments in the aerospace industry. Both form porous stable oxide layers with an open honeycomb structure topped with some protrusions which provides for good mechanical interlocking [9, 26]. Humid environments have been proven to decrease the adhesion strength of both FPL etched and anodised surfaces, with failure occurring within the aluminium oxide layer, which had changed from the original amorphous oxide layer to a hydrated layer with a semi-crystalline structure [26]. Water does not necessarily result in decreased adhesion though, Arslanov and Funke found that the strength of adhesion of epoxy coatings on aluminium increased after an initial decrease when aluminium was aged in water. Coupons with a hard polymer film

had a 25% increase in adhesion strength after four weeks immersion of the aluminium coupons in water , whilst coupons with a soft polymer film had a 500% increase in adhesion strength for the same immersion time compared to coupons that had not been aged. This was shown to be the result of $AI(OH)_3$ on the surface enabling stronger chemical bonds between the epoxy resin and the aluminium surface [4].

Boehmitising of an aluminium surface is sometimes referred to as hydro-thermal treatment, as it is accomplished by the immersion of the aluminium in boiling water [27]. Immersion of aluminium in boiling water transforms aluminium tri-hydroxides to boehmite, a porous oxy-hydroxide [28] and has the chemical form AIOOH. Boehmite is a meta-stable phase on the aluminium-water equilibrium phase diagram, shown in Figure 2.4, and requires temperatures of over 300°C for dehydration to begin, complete conversion requires temperatures well above 300°C [22]. The thickness of the boehmitic oxide is proportional to the period of time it is immersed in the boiling water.

In aluminium alloys containing magnesium, the magnesium will preferentially diffuse to the surface upon thermal treatment, resulting in a significantly higher magnesium concentration on the surface than in the bulk [27, 29, 30]. Thermal treatment results in partial crystallisation of the aluminium oxide layer, and the boundaries between amorphous and crystalline regions form pathways through which magnesium diffuses to the surface of the oxide layer and oxidises [22, 27]. Magnesium oxide surfaces are therefore going to play a part in the bonding of any coating to a thermally treated aluminium-magnesium oxide surface. Magnesium oxide surfaces formed in ambient conditions are generally a combination of magnesium oxide, hydroxide and strongly bonded hydrates [31, 32]. The oxide/hydroxide layer of magnesium oxide formed at ambient conditions was found to be amorphous MgO and Mg(OH)₂ platelets by transmission electron microscopy [33]. The presence of magnesium oxide on the surface of aluminium alloys was found to increase the hydration rate of the alloy, and this increased hydration for a given time period was found to improve adhesion of ethylene copolymers to the substrates [27]. This indicates that the presence of magnesium oxide on the surface of some substrates due to thermal treatment will be beneficial to adhesion, and at worst will have no negative effect of the bonding of PEEK to pretreated aluminium 5052 substrates.

In summary, water is essentially present on aluminium oxide surfaces in one of three states, physisorbed, chemisorbed, or chemically bound. Physisorbed water is atmospheric moisture that has adsorbed weakly to the surface and can be removed by

heating the substrate to 100°C, this is the superficial contamination shown in Figure 2.1. Chemisorbed water is bound to the aluminium oxide on the top surface as hydroxide ions, no more than a few molecular layers thick and able to be removed by thermal treatment between the temperatures of 100°C and 200°C depending on the bonding. The chemisorbed water exists in the segregation layer in Figure 2.1. The chemically bound water is present as a bulk layer of aluminium hydroxide and or aluminium oxyhydroxide. This layer is typically nanometres thick and is represented by the hydration – hydroxylation layer shown in Figure 2.1. Removal of this water requires significant thermal energy, varying depending on the phase of aluminium hydroxide or oxyhydroxide, and follows the phase transformations presented in Figure 2.3.

2.2 Adhesion of organic compounds to aluminium surfaces

The adhesion of organic compounds onto aluminium substrates has been studied in relation to the packaging industry, the bonding of sealed aerospace joints and the application of organic coatings such as paint to prevent corrosion of structural aluminium components. The principles that apply to adhesion of organic compounds to aluminium in these industries will also apply to the adhesion of thermally sprayed PEEK on aluminium substrates. There are two key factors that affect adhesion, contact area between the organic compounds and substrate, and the bonding between the organic compounds and the substrate where contact exists [26, 34, 35]. The degree of intimate surface contact is affected by the presence of contaminants at the surface, either in the form of rolling grease or similar organic compounds from manufacturing processes, or adsorbates from the environment, predominantly adsorbed water. These contaminants at the surface can result in void spaces between adhesive and substrate, resulting in lowered contact area for adhesion and can act as failure initiation points [34]. Intimate surface contact between substrate and adhesive is also influenced by the surface free energies of the substrate and adhesive, and the wetting angle of the adhesive on the substrate. The lower the wetting or contact angle, the greater the wettability of the surface, resulting in the adhesive being able to flow into pores and other morphological surface features [34, 35].

Where intimate surface contact is achieved there are a number of potential ways that bonding can occur. The most basic is through mechanical interlocking, where the adhesive conforms to irregularities in the substrate surface [35]. Bonding between adhesive and substrate can take on many forms, including covalent bonding, Van der Waals interactions, hydrogen bonding, dipole-dipole interactions, dispersion forces and electron pair sharing interactions [34, 35]. Bonding of organic compounds to aluminium

substrates generally occurs through dipole interactions, dispersion forces, hydrogen bonding, and electron pair sharing [26]. Permanent dipoles exist when a highly electronegative atom is bonded to a less electronegative atom, resulting in the more electronegative atom being slightly negatively charged and the less electro-negative atom being slightly positively charged. A positive dipole atom on a substrate can then attract a negative dipole atom on an adhesive, forming a weak bond. Electron pair sharing can also occur, where a Lewis base with a non-bonded electron pair, can act as an electron donor, and attract a Lewis acid which is electron deficient [34]. Dispersion forces are the forces that result from instantaneous dipoles existing between molecules, also referred to as Van der Waals forces, where an instantaneous imbalance of electrons around an atom, induce an dipole between it and a neighbouring atom, referred to as an instantaneous dipole-induced instantaneous dipole interaction [34].

The bonding of organic molecules to aluminium surfaces with different pretreatments has been investigated by van den Brand et al. through Fourier transform infra-red (FTIR) spectroscopy, FTIR reflection absorption spectroscopy (FTIR-RAS), and x-ray photoelectron spectroscopy (XPS). The five pretreatments used on the aluminium surfaces were characterised for hydroxyl concentration at the surface with XPS. Model compounds were exposed to the surface and bonding of the compounds investigated through FTIR and FTIR-RAS [14, 36, 37]. Ester functional groups were found to bond to the aluminium through the carbonyl group forming a Lewis acid-base pair with hydroxyl groups and incompletely co-ordinated cations on the aluminium substrate, hydrogen bonding between the esters and the oxide surface was also evidenced by the relationship of ester to hydroxyl concentration on the aluminium surface [37]. Similar results were found for the bonding of anhydrides and carboxylic acids to aluminium surfaces, with the additional bonding through carboxylic groups, where a carboxylic group would be deprotonated, and bonded to a hydroxyl or water molecule chemisorbed on the aluminium surface [36]. These studies showed that organic molecules can and do form chemical bonds to aluminium oxide surfaces, that bonding occurs through hydroxyl groups and incompletely co-ordinated cations on the surface of the aluminium oxide layer. PEEK has ether and carboxyl groups in the polymer chain, providing potential for chemical bonding between PEEK and aluminium surfaces.

2.3 Surface chemistry of aluminium by XPS

X-ray photo-electron spectroscopy is a spectroscopic technique that provides information about the elements present in the surface layer of a sample and their chemical state and has been used extensively to study aluminium surface oxides. The information directly List of research project topics and materials 10 gathered by XPS is the number and energy of the secondary electrons being emitted from the sample after the sample is exposed to x-ray radiation of a fixed wavelength. Because XPS involves the measurement of electron energies it is necessary to conduct the experiment under ultra high vacuum, thus it is important for samples to be vacuum compatible.

X-rays are focussed onto the surface of the sample, where they interact with the top several microns of the material. Incident x-rays can cause electrons to be excited to a higher orbital, and when they fall to their original orbital release a photoelectron, as illustrated in Figure 2.5. The kinetic energy of the released electron can be related to the binding energy of the electron in the atom, and the energy of the x-ray, as shown in equation 2-1.

Equation 2-1	BE = hv - KE	where	BE is the binding energy
			KE is the kinetic energy
			$h_{\rm V}$ is the energy of the x-ray
			h is Planck's constant, 6.626 x 10 ⁻³⁴ m ² kgs ⁻¹
			\boldsymbol{v} is the frequency of the x-ray

The x-ray energy, hv is constant (as for a monochromatic x-ray source) so the equation can be used to derive the BE of the electron from the kinetic energy measured by XPS. The energy of x-rays from a magnesium x-ray source was 1253.6 eV, and from an aluminium x-ray source was 1486.6 eV. Knowledge of the binding energies allows the elemental composition of the sample to be determined as each element has a unique set



Figure 2.5 Schematic of the basic principle of XPS analysis.

of binding energies. The binding energies of elements are, however, subject to variations depending on the bonding of the element. If an element is bound to a highly electronegative element it can cause an increase in the binding energies associated with the bonding element. Peaks often end up partially superimposed upon one another. In that instance peak deconvolution with appropriate software can be used to separate the peaks and determine the chemical states present and the relative quantities, in relation to peak area. Wide scans are low resolution scans that reveal the elemental makeup of the surface of the specimen, as shown in Figure 2.6. This gives information as to what elements are there, and the percentage of the different elements present. A narrow scan is a high resolution scan, generally over 20 to 30eV. Narrow scans reveal the shift in binding energies resulting from different species of a given element. For example, Figure 2.6 shows a typical O 1s narrow scan with three distinct oxygen binding energies resulting from oxygen bound in three distinct forms, in this case aluminium oxide, aluminium hydroxide and water. The different strengths of the bonds between aluminium and oxygen in the aluminium oxide and aluminium hydroxide result in different photoelectron binding energies as measured by XPS, similarly the bonds between oxygen and hydrogen in water are different, thus three distinct peaks are present in the O 1s narrow scan. To reference the absolute position of the O 1s peaks, or any other narrow scan peak, a narrow scan of the adventitious carbon peak is always performed so that the exact position can be determined relative to the carbon peak. This allows determination of the shift of the spectrum due to any static charging of the sample, which occurs if it is inadequately grounded, or is an electrical insulator.

The study of the surface chemistry of aluminium by XPS has been undertaken by many authors with much work published on the subject [6, 19, 20, 27, 29, 38-47]. Key factors of research into aluminium oxides and hydroxides include finding reference peaks of known widths and positions, knowing the separation of the common peaks, and deconvolution of multiple superimposed peaks to find the ratios of different species of an element present.

There are two primary regions of interest when considering XPS analysis of aluminium surfaces, the O 1s spectra and the Al 2p spectra.



Figure 2.6 A characteristic wide scan revealing elemental composition, and a narrow scan of the O 1s peak with peak deconvolution (this work).

The O 1s spectra changes dependent on the species of oxygen present. References of known samples of gibbsite, boehmite and corundum were analysed and the peak positions and separations recorded [38, 39, 43, 44]. These references provided absolute positions for oxygen peaks in aluminium hydroxide, aluminium oxyhydroxide, and aluminium oxide to be established. The result of this research into XPS of aluminium surfaces was that three peaks could be resolved in the O 1s spectra, one each belonging to $O^{2^{-}}$ species, OH^{-} species and chemisorbed water species (H₂O with a permanent dipole bond). XPS cannot give phase information, therefore cannot be used to distinguish between gibbsite and bayerite, nor can it determine the difference between a boehmitic surface and one which is 50% gibbsite (Al(OH)₃) and 50% corundum (Al₂O₃). Despite these limitations, knowing something of the aluminium-water phase diagram and the processing steps used to prepare a sample, the surface chemistry of samples can be assessed and differences between different treatments shown.

A key factor that complicates the analysis of the O 1s spectra is that the three characteristic peaks overlap one another. To enable the relative ratios of the three characteristic peaks to be determined a process known as peak deconvolution is performed. Peak positions and shapes are determined by running known standards in

the XPS and with reference to literature. Peak positions and separations as found in literature are displayed in Table 2.1.

The work performed by Lopez et al. [45] and McCafferty and Wightman [38] fitted a peak in the O 1s spectra for the chemisorbed water on the aluminium surface, resulting in more robust data than that where chemisorbed water on the aluminium surface was not taken into consideration. As a result, this study used the peak separations used by Lopez et al. for peak fitting the O 1s spectra. Lopez et al. [45] fitted four peaks, O^{2-} , chemisorbed water, a boehmitic OH^- (+1.2eV) and a gibbsitic OH^- (+0.9eV) peak. Due to the low intensities of the gibbsitic hydroxide peak and its close position to the boehmitic hydroxide peak it was not fitted separately in this work, but a combined hydroxide peak, similar to McCafferty and Wightman's was fitted.

The Al 2p oxide peak position can vary due to a change in Fermi level according to Lopez et al., with an increase in surface acidity corresponding to an increase in Al 2p binding energy.

Once peak shape and position have been determined, deconvolution is a matter of adjusting peak heights, full widths at half maximum height, and positions within restricted limits such that the sum of the intensities of the three components resemble the O 1s spectra collected from the aluminium surfaces. A representative deconvoluted spectrum is presented in Figure 2.7.

Authors	O ²⁻ position	OH ⁻ position	Chemisorbed water	O ²⁻ to OH ⁻ peak
	(eV)	(eV)	position (eV)	separation (eV)
This study	Varies	+1.25	+2.2	1.25
McCafferty and Wightman [38]	531.8	532.9	534.3	1.1
Strohmeier [20]	531.3	532.8	Not considered	1.5
Nylund and Olefjord [19]	531.1	532.8	Not considered	1.7
Lopez et al. [45]	Varies	+1.2	+2.0	1.2

Table 2.1 Published oxide and hydroxide peak positions.



Figure 2.7 A representative O 1s XPS spectrum with deconvoluted components. Green is the O^{2-} peak, blue the OH⁻ peak, and red the chemisorbed water peak (this work).



Figure 2.8 Left, XPS narrow scan spectra of the Al 2p peaks of a thin oxide layer. Right, a thick oxide layer (this work).

Analysis of Al 2p spectra provides two key pieces of information, the ratio of metallic aluminium to oxidised aluminium, and the separation of the Al⁰ peak and the Al³⁺ peak. The ratio of the metallic aluminium peak to the oxidised peak enables the thickness of the oxide layer to be estimated as the photo-electrons can only escape through a certain depth of a material of given density. Two representative Al 2p spectra are presented in Figure 2.8. The ratio of intensities of each Al 2p peak can then be used to determine the thickness of the oxide layer using equation 2-2.

Equation 2-2
$$t = \lambda_0 \ln \left(1 + \frac{N_m}{N_o} \frac{\lambda_m}{\lambda_o} \frac{I_o}{I_m} \right)$$
 [20],

where *t* is the oxide thickness in angstroms, N_o and N_m are the volume densities of aluminium atoms in the oxide and metal respectively. Similarly I_o and I_m are the areas of oxide and metal peaks and λ_o and λ_m are the inelastic mean free paths of the Al 2p photoelectrons in the oxide and metal. This formula simplifies to equation 2-3.

Equation 2-3 $t = 24 \ln \left(1 + 1.4 \frac{I_o}{I_m} \right)$

It has been shown by Jeurgens et al. [48] that the above technique can have quantitative inaccuracies of up to 20%. This technique does, however, provide a reliable comparison of thickness between individual samples and treatments, despite quantitative inaccuracy, and as such will be sufficiently accurate for this work.

The different Al³⁺ peaks as generated by Al bonded to O²⁻, as opposed to OH⁻ or chemisorbed water cannot be deconvoluted as they do not have significant separation from each other and the resolution of XPS is not sufficient to allow for individual interpretation of these peaks. The separation of the oxide peak from the metallic peak is typically 2.6eV if the oxide is grown as an amorphous passivating oxide, but the separation can be up to 3.4eV if the oxide is grown as an amorphous anodic oxide [20]. Other oxide layers have binding energies central to this range, resulting in several possible oxide formations within a range of 0.8eV, irresolvable with XPS resolutions.

The separation of the O 1s oxide peak from the Al 2p metallic peak gives an indication of the basicity/acidity of the oxide layer on an aluminium surface [41, 43, 45, 46]. This comparison was attempted in this research but due to a lack of resolution and bias charging of the substrates of interest no significant results were generated.

Mullins and Averbach correlated the aqueous point of zero charge (pzc) to Fermi levels and O 1s peak positions for various metal oxides [44]. The lower the pzc the more acidic a surface is, the higher the pzc, the more alkaline the surface is [44]. Further work on chemically treated aluminium surfaces found that XPS could be used to determine the Al 2p oxide peak, this position was used to calculate the Fermi level of the bulk standards and chemically treated surfaces, and the Fermi level used to calculate the pzc. It was reported that boehmitic surfaces have a high pzc, and are therefore basic, whilst acid etched surfaces have a low pzc and are therefore acidic [44]. Fermi levels have been further used to classify surface acidity of treated aluminium surfaces. The surface basicity of the following set were determined to be: boehmitic layer > thermal oxide > alkaline degreased surface > as cold rolled [1]. Lopez et al. verified and built on the work of Mullins and Averbach comparing treated aluminium surfaces with XPS and x-ray absorption near-edge studies (XANES) analysis. They also showed that plotting Al 2p oxide peak position against O 1s O²⁻ peak position enabled determination of surface basicity, with basicity results: boehmitic surface > annealed > NaOH degreased > phosphoric acid anodized > detergent degreased [45].

XPS is useful in this work as it is a surface sensitive technique, capable of analyzing the top 10 nm of a material. Since adhesion occurs at the interfacing molecular layers, it is the chemistry of the surface that controls adhesion. Aluminium oxidizes very rapidly, hence adhesion to aluminium substrates is actually adhesion with an aluminium oxide layer. Due to the high affinity of water to aluminium oxides, aluminium oxide layers are typically comprised of aluminium oxides, hydroxides and oxyhydroxides, in addition to adsorbed and chemisorbed water molecules. By analyzing the binding energies of the oxygen molecules present in the oxide layer, XPS can be used to determine the ratio of oxygens with two bonds to aluminium molecules (in the case of aluminium oxide) to the number of oxygens with one bond to an aluminium molecule (in the case of hydroxide) and those oxygen molecules which are bonded as chemisorbed water. XPS is limited though as it cannot differentiate between the hydroxide in aluminium oxyhydroxide (behmite) and that in aluminium hydroxide, nor can it differentiate between the oxide in aluminium oxide.

XPS can also be used to determine the thickness of an oxide layer up to ~10 nm. This is achieved by comparison of the metal and oxide peaks of the Al 2p spectrum. The ratio of the oxide to metal peaks increases with oxide layer thickness, but as photo-electrons cannot escape from depths greater than 10 nm from the surface, thicker oxide layers will get no metal peak, and as such no comparison can be made from the XPS data. Both the thickness limitations and the inability to differentiate aluminium oxyhydroxide from aluminium hydroxide and oxide respectively can be overcome by also employing Rutherford Backscatter techniques.

2.4 Thermal spray of polymers

2.4.1 Thermal spray processes

Thermal spray is a method of producing a coating that strongly adheres to the substrate. Fine particles are fed into a hot accelerating jet where they are melted and accelerated towards the substrate. The particles then impact the substrate and form "splats," which build up to form a continuous cohesive coating. Varying the spray parameters achieves low porosity and void content, as well as improving the contact area between the splats and the substrate.



Figure 2.9 Schematic of a typical plasma spray system [50].

There are a number of different thermal spray application techniques. They can be divided into four sub groups, combustion spraying, plasma spraying, cold spraying and wire arc spraying, but wire arc cannot be used for polymers as it requires conducting consumable electrodes [49].

Plasma spraying passes a direct current arc between two electrodes to superheat an inert gas (typically argon or an argon-hydrogen mixture) to temperatures in the range of 6000°C to 15000°C [50]. A powder is carried into the plasma jet in a stream of inert carrier gas (often nitrogen) and the powder is heated and accelerated by the jet onto the substrate at velocities which typically range between 200 ms⁻¹ and 400 ms⁻¹ [51]. The powder is fed into the plasma jet at a position and angle such that the particle flight path maximises heat transfer and velocity required for the coating parameters required. Excessive time in the plasma plume can result in thermal degradation of the sprayed particles. Degradation can be in the form of thermal cracking of the polymer chains or oxidation or hydrolysis of the polymer chains, although these are less common for this technique as the plasma tends to be relatively free of oxygen and water, and it is only that water which has been adsorbed onto the polymer powder feedstock that can cause oxidation or hydrolysis [52]. A schematic of a plasma system is shown in Figure 2.9. Plasma spraying of polymers is discussed more fully in section 2.4.5.

Cold spray accelerates powders to speeds between 300ms⁻¹ and 1200ms⁻¹ using gas dynamic techniques. Nitrogen and helium are the process gases used in the cold spray technique. The term cold is used because the gas temperatures used vary between 0°C and 800°C, much lower than the temperatures achieved in conventional thermal spray techniques [50]. Cold spraying is not suitable for the formation of polymer coatings (or other low density powders) as the low density particles do not have sufficient mass to penetrate the bow-shock pressure zone that forms where the gas stream impinges on the substrate [50].

Combustion spraying includes three different subgroups, high velocity oxygen fuel and high velocity air fuel (HVOF and HVAF respectively), flame and detonation spraying. Flame spraying uses an external combustion flame into which either powder or wire is fed. For polymer spraying, the powder is fed into the flame (flame temperature 3000 to 3350K with a velocity of 80 to 100 ms⁻¹) [49]. Residence times with flame spraying are comparatively long due to the low velocity of the particles and the flame.

Detonation spraying uses a charge of acetylene, oxygen, and powder in a combustion chamber which is then detonated by a spark. The heat of the combustion and the combustion products melt the powder and the detonation wave propels the particles towards the substrate. After each detonation the chamber is purged by nitrogen. The frequency is typically 4 to 15Hz. Detonation spraying operates at temperatures up to 4500K (depending on fuel composition) and accelerates particles to speeds of between 750 and 900ms⁻¹ [49]. Detonation spraying has typically been used for tungsten carbide cobalt coatings and aluminium oxide coatings. As with cold spray, detonation spraying is unlikely to be useful for polymer coatings due to low particle densities resulting in insufficient particle mass to penetrate the bow shock region above the substrate.



Figure 2.10 A schematic of the Browning Aerospray 150, the HVAF thermal spray gun used in this research.



Figure 2.11 A Schematic of a typical high velocity thermal spray system [50].

HVOF and HVAF employ continuous combustion in an internal combustion chamber where oxygen or air is combusted at high pressure with hydrogen or a gaseous hydrocarbon (often propane) in the case of HVOF and with kerosene or a gaseous hydrocarbon in the case of HVAF. The powder is fed into the combustion jet which operates in the range of 3000 to 3500K and accelerates particles to velocities of 200 to 1000ms⁻¹ [53]. HVOF and HVAF spraying allow the formation of coatings with lower porosities than plasma spraying due to the higher velocity of the particles on impact, although optimised plasma systems can achieve very low porosities [50]. A typical HVOF gun is shown in Figure 2.11, and a typical HVAF system in Figure 2.10. High velocity thermal spray of polymers is discussed in more detail in section 2.4.7.

HVOF thermal spray guns burn a hydrocarbon fuel with oxygen, whereas HVAF guns burn the fuel with compressed air. This results in HVOF having a higher temperature gas jet with a stronger oxidising environment than HVAF. The higher temperatures of HVOF guns require water cooling, where in comparison many HVAF guns rely on cheaper air cooling. In the schematics of HVOF and HVAF spray guns, two different powder feed orientations are shown, radial (Figure 2.10) and axial (Figure 2.11). Powder feed geometry is unique to each thermal spray gun and is not specific to a certain type of gun, some HVOF guns use radial feed, there is no reason for an HVAF gun not to use axial feed. Both HVAF and HVOF spraying results in supersonic shock diamonds in the gas jet due to the supersonic flame velocity. Because HVAF burns compressed air instead of oxygen, the flame not only has a lower temperature, but also there is a significant List of research project topics and materials 20 portion of nitrogen in the combustion gases. The combination of these two factors results in HVAF guns having a cooler, less oxidising flame, which will result in less thermal degradation of polymer particles. There have been far fewer HVAF gun designs than there have been HVOF designs. Praxair developed the Jetstar system for spraying of tungsten carbides, Browning developed the Aerospray, and UniqueCoat developed an aided combustion HVAF gun, the Intelli-jet, the only HVAF system currently being manufactured [51, 54, 55].

2.4.2 Microstructure of polymer coatings

A thermal spray coating is unique in the way it is formed and its microstructure. In contrast to coating techniques such as chemical or physical vapour deposition which build up the coating atomically, thermal spray builds up a series of particles in the range of 5µm to 200µm diameter, generating a thicker coating faster. The particles are entrained in a high temperature gas (or plasma) jet and accelerated towards the substrate. The particles are heated to a plastic or molten state and obtain a high kinetic energy in the range of 1 x 10^{-7} J to 1 x 10^{-5} J (for a plasma or high velocity system, note that individual particles have a mass of 5 x 10^{-12} kg to 5 x 10^{-10} kg). On impact, the particles deform and spread on to the substrate or on the top of previously deposited material or "splats". The morphology of a splat after impact is a result of factors including the degree of melting achieved during flight, the particle viscosity, the particle velocity, substrate temperature and substrate morphology [53]. Common splat forms for polymer splats include disc, fried egg and splashed or fingered morphologies [53, 56]. Disc splats, of which fried egg splats are a sub group, tend to result in coatings with high adhesion and cohesion with low coating porosity, while conversely, coatings formed from splashed splats have high porosity and poor adhesion and cohesion [53, 56-58].

Adhesion refers to the force required to remove a coating from a substrate, and a coating with high adhesion will require a greater force to separate the coating from the substrate than a coating with low adhesion. Cohesion refers to the internal strength of a coating (or the adhesion between individual splats). If a coating has high adhesion, but poor internal strength, when placed under shear or tension it is likely to fail within the coating, or as a cohesive failure. If a coating has high cohesion, but poor adherence to the substrate, it is likely to peel off the substrate, leaving a clean substrate behind, referred to as adhesive failure [34]. Adhesion can be quantified through three techniques, peel tests, tensile tests and shear tests. A peel test works by measuring the force required to peel the coating off a substrate, as illustrated in The most suitable quantification method for thermal spray



Figure 2.12 Schematic of the different adhesion quantification methods, a) peel test, b) tensile test, c) shear test.



Figure 2.13 Left, optical micrograph of a plasma sprayed PET coating [59]. Right, schematic of splat build up in thermal spray. The black spots represent porosity from degassing and poor wetting.

coatings is the peel test, where the coating is peeled off the substrate by attached tabs, and the force required for separation is recorded [34]. In tensile tests, pull tabs are affixed to the substrate and coating through an epoxy or similar adhesive, and the force required to cause adhesive or cohesive failure of the coating is recorded per unit area of the coating [34]. A shear test has tabs affixed in a similar manner as in a tensile test, but the force is applied in shear as opposed to in tension, as indicated in Figure 2.12 [34].

In Figure 2.13 a micrograph of a thermally sprayed PET shows how the splats build up. This is especially noticeable at the interface between the polymer and the substrate (bottom of micrograph). The dark spots represent voids in the coating.

It is noticeable that there is greater definition between splats near the interface with the substrate, and no discernable definition between splats at the surface, this is probably

due to increased heating of the substrate by this point of the coating procedure, thus providing more heat to achieve full melting of the splats.

A number of spray and substrate variables affect how well the splats adhere to the substrate and each other, as well as the microstructure of the coating. The resistance of a coating to wear and corrosion is closely related to the microstructure. Coatings with high density (low porosity) typically provide better corrosion and wear resistance. Thermal barrier coatings require porosity on the order of 10% to enable thermal expansion of the coating. Adhesion of the coating to the substrate is improved by increased surface area for bonding through grit blasting. Similarly low coating porosity increases the surface area available for both chemical and mechanical bonding.

The thermal history of a coating and the particles it is formed of will determine whether a polymer coating is amorphous or semi-crystalline. Coatings that quench through the glass transition point of the polymer will be amorphous, whilst coatings that cool slowly through the glass transition temperature are likely to be semi-crystalline [53]. The amorphous/semi-crystalline transition is normally associated with a corresponding decrease in specific volume, thus semi-crystalline coatings have a degree of residual stress. Whilst amorphous coatings will have low residual stresses compared to semi-crystalline coatings, amorphous coatings exhibit reduced wear resistance and increased permeability, resulting in poor corrosion resistance [53].

2.4.3 Spray variables

The degree of fusion, or the degree to which the particle melts is an important parameter when thermally spraying any material. It affects how well the splat can deform to match the surface it hits. That is important both for the mechanical interlocking of the interface as well as the surface area available for chemical bonding with the substrate. A high degree of fusion also generally leads to dense coatings with low porosity, making them better for corrosion resistance [52] but may also result in degradation of the particles, especially in those particles with low thermal conductivities.

The degree of fusion is dependent on the heat transfer from the combustion gases or the plasma, and the thermal conductivity of the polymer particle. Because of the low thermal conductivity of the polymer particles, the centre of a polymer particle has a significantly lower temperature than the surface. Transferring enough heat to the centre of a particle can, however, lead to thermal degradation of the surface [56, 60, 61]. Thermal degradation takes the form of thermal cracking, oxidation, and hydrolysis of the polymer

chains. This can lead to cracking of the polymer chains and/or cross linking, both of which can lead to embrittlement of the polymer [52, 62]. Too little heat transfer results in the centre of the particles remaining solid or highly viscous. This results in coatings with poor contact between polymer splats and the substrate and large voids between unmelted polymer splats. This results in poor mechanical interlocking and low surface area over which chemical bonds can form [53, 56, 58, 60, 61]. Residence time in the jet and particle velocity are two critical factors that are inextricably linked to thermal degradation. Residence time is affected by particle velocities, particle trajectory through the spray plume, spray distance, and powder feed position. As previously mentioned, it is critical that the right amount of heat is transferred to the polymer particles. As such, the residence time of the polymer particles must be understood and adjusted so as to obtain the optimum heat transfer. In plasma and combustion thermal spray processes the high temperature jet (be it a plasma plume or combustion flame) has a thermal profile that varies both with axial position from the nozzle as well as radially from the centre of the jet. As such, it is important to know particle trajectories and velocities so heat transfer to the particles can be considered and kept to an optimum level [52, 53].

The particle velocity is defined by the spray technique and parameters, but the spray distance, powder feed position, and powder feed angle have a degree of variation in them. Particle velocity not only affects residence time but also the kinetic energy with which particles impact the substrate, which is then transformed into heat energy [52, 56, 60, 61].

Spray variables are one factor which determine the deposition efficiency of a thermal spray process, although substrate variables and the powder being sprayed all influence the deposition efficiency of a process. Deposition efficiency refers to the fraction of powder sprayed by mass through a thermal spray torch that is deposited on the substrate, or in other words, the mass gain of the substrate as a fraction of the total mass of powder sprayed. Comparisons between the different thermal spray systems are difficult due to the large number of variables affecting deposition efficiency, and especially the dependence on particle and substrate material.

2.4.4 Substrate variables

If the polymer does not wet the substrate well, due either to poor compatibility with the substrate or thermal degradation of the polymer, the splats will have high contact angles with the substrate. This will be a barrier to good overlapping coverage and will result in

the inclusion of voids at the polymer/substrate interface as well as poor surface contact. This will lead to poor adhesion of the polymer coating [53, 58, 61].

The roughness of a substrate is known to affect the adhesion of coatings. Roughness can be quantified in a number of ways, the most common of which are Ra and skewness (Sk). Ra is determined to be the average roughness area between the roughness profile and the mean line of the surface, or the integral of the absolute roughness profile [63]. The limitation of Ra values is that two or more distinctly different surfaces can have the same Ra value as shown in Figure 2.14. Skewness (Sk) is determined by the symmetry (or lack of) of the roughness profile around the mean line. Thus, a surface which is essentially flat with pits in it has a negative Sk, whilst a surface with protrusions from the average plane has a positive Sk, as shown in Figure 2.15. Surface roughness and skewness are generally measured with surface profilometers, in this work an AFM was used to generate the surface profiles from which Ra and Sk were calculated.

Ra is calculated according to equation 2-4, and skewness is calculated according to equation 2-5.

Equation 2-4 $Ra = \frac{1}{n} \sum_{i=1}^{n} |z_i|$

Equation 2-5 $Sk = \frac{1}{nR_q^3} \sum_{i=1}^n z_i^3$

Equation 2-6
$$R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n z_i^2}$$

The set of numbers of i = 1 through n is the set of measurements made across a substrate, either from a straight line or from a grid array. z_i is the vertical displacement of the substrate from the mean substrate height. R_q is the root mean square surface roughness, calculated with equation 2-6 and used in equation 2-5 to calculate skewness of a surface.

All thermal spray processes result in significant heat transfer to the substrate from the thermal spray torch. Heat transfer to the substrate not only affects the substrate temperature, but also potentially results in heat treatment of the substrate and of the coating [50]. Especially important for polymers is the temperature of the substrate relative to the glass transition temperature of the polymer, altering the crystallinity off the coating, and the associated mechanical properties associated with semi-crystalline and amorphous polymer coatings [53]. Higher temperature substrates allow splats to flow



Figure 2.14 Schematic illustration of two surfaces with different surface profiles but the same Ra value.



Figure 2.15 Schematic illustration of a) a surface with negative Sk and b) a surface with positive Sk.

well, forming good disk shaped splats, whereas low temperature substrates can cause splats to cool too quickly, resulting in splashes and poor coverage with a large void fraction [50]. However, a cool substrate and fast splat cooling will also lead to an amorphous polymer, which can be desired, as higher temperature substrates lead to slow cooling leading to semi-crystalline coatings. As the coatings crystallise they go through a change in properties and sometimes contract, this can lead to residual stress in the coating, and sometimes this stress cracks the coating [59].

Substrate preparation also affects the wettability and adhesion of the polymer to the substrate. Substrates can either be chemically or physically prepared, or sometimes, both. Traditionally in the aerospace industry, surfaces are either etched or anodised, or a conversion coating is applied to the surface to improve adhesive bonding [8, 9]. The printing and labelling industry typically either applies a conversion coating to aluminium surfaces or exposes them to a plasma source before application of labels or coatings [2, 4, 5, 7-10, 35]. Both industries perform these preparatory steps to improve adhesion

through chemical bonding between the adhesive or coating and the aluminium substrate [7-9]. Meanwhile in thermal spray, most surfaces are simply degreased with a solvent and then grit blasted before being sprayed [53, 61]. Degreasing is important so as to prevent the grease from substrate processing steps from interfering with the Lewis acid-base interactions of the polymer splats with the metal substrate [41]. Grit blasting increases the surface contact area and variation from the average condition. This enables good mechanical interlocking of the polymer to the substrate and also a high surface area over which chemical bonds can form [62]. It is probable, however, that chemical bonds can form between a thermally sprayed coating and its substrate. As previously shown, other coating and adhesive industries already chemically prepare a surface to improve bonding. It is probable that tailoring the surface chemistry of a substrate could improve the number of sites available for chemical bonding and thus improve adhesion of coatings to the substrate.

2.4.5 Polymer single splats

The only published work dedicated to polymer single splats has been focussed on HVOF spraying of polyimides and Nylon-11 [56, 64, 65]. The polyimides were sprayed with an HVOF Jet Kote II system and deposited on a polymer matrix composite substrate. The significant results from the polyimide spraying was substrate pre-heating resulted in well melted splats, with increased deposition efficiency and improved adhesion to the substrate [64]. The imaging of single splats was performed with splats sprayed on glass substrates, not the substrate of interest, with significantly different material and thermal properties. Adhesion of the coatings was not quantified, and the reported improvements only represented that the coatings did not disbond from heated substrates upon cooling [64]. HVOF spraying of Nylon-11 (by Jet Kote II system) has been modelled, and the models compared to experimental data. Nylon-11 splats deposited on smooth room temperature substrates were found to have a "fried-egg" morphology with a cool viscous core in the sprayed particle resembling the yolk of a fried egg upon impact. Spraying onto substrates heated to 190°C (the melting point of Nylon-11) resulted in splats that resembled disc splats achieved when spraying metals onto pre-heated substrates [56]. These substrates were however heated to the polymer melting point, so post impact melting is likely to have occurred. Deposition of splats on rough surfaces resulted in increased fingering and instability in the flow of the splats upon impact. Splats were found to have good contact with the substrate under the core of the splat, but in the thin areas of the splat, the radial flow parallel to the surface resulted in poor contact with the substrate in this area [65]. As with the polyimide splats, adhesion was not quantified, but gualitatively assessed based on the degree of intimate contact with the substrate. As can
be seen, there is very limited literature available about polymer single splats. The effect of surface temperature and roughness has been lightly touched upon, and the effect of surface chemistry not at all. This work will answer in depth the effect of substrate temperature, morphology and chemistry on PEEK single splats. Spreading of single splats of all materials is discussed in more detail in section 2.5.

2.4.6 Plasma spray of polymers

Polymers that have been investigated in conjunction with plasma spraying include poly(methyl methacrylate) (PMMA), polyamides, poly(ethylene terephthalate) (PET), poly(phenylene sulphide) (PPS), poly(aryl ether ether ketone) (PEEK), and medium density polyethylene (MDPE) in conjunction with ceramic fillers [52, 59, 66-68].

Plasma arc power was found to have a very strong correlation with the adhesion of the polymer to the substrate. The higher the arc power the greater the adhesion of the coating [66]. It was also found that for the spraying of PMMA by plasma spray the ideal spray distance was about 100mm, at an optimum arc power of 22kW, with decreasing adhesion for spray distances both shorter and longer [66]. For both polyamide and PMMA it was found that poor true contact area between the polymer and the substrate resulted in low adhesion while high true contact area resulted in higher adhesion values. Bao, Gawne and Zhang [66] also found that moderate heating of the substrate resulted in higher adhesions, but that excessive heating was detrimental to coating adhesion, with results indicating thermal degradation of the polymer when the substrate was held at high temperatures. The same authors reported that there was a critical gun traverse speed for plasma spraying of PMMA powders such that the deposited polymer layer was not overheated by the plasma jet [52]. This was determined by measuring the weight loss of the polymer coating when exposed to the spray jet without a powder feed. Strait and Jamison plasma sprayed PEEK onto carbon fibre reinforced PEEK composite substrates for the purpose of coating medical implants [68]. Greater thermal energy transfer from the spray torch to the substrate was found to result in a darker coating with increased adhesion of the coating to the substrate. Decreasing the spray distance (hence increasing thermal transfer to substrate) increased adhesion by 37 – 63%, whilst cooling of the substrate by high velocity air jets resulted in a 60 – 67% decrease in coating adhesion [68]. Thermo-gravimetric and differential scanning calorimetry revealed no significant degradation of the "hotter" coatings, despite the darker colour observed in the "hotter" coatings. The plasma spray process was shown to produce generally amorphous coatings, with post spray annealing increasing the crystallinity of the coatings. Coating crystallinity was found to have no affect on coating adhesion, and although increased

crystallinity was expected to increase coating toughness and wear resistance no tests to confirm this hypothesis were performed [68].

In an attempt to spray polymers with low thermal decomposition temperatures (below 300°C) Henne and Schitter [67] investigated the use of high speed plasma spraying, that accelerated the particles at up to 600ms⁻¹ and the use of an external injector such that the polymer particles entered the plasma plume in a cooler region. It was found that the lower temperatures of these molten polymers resulted in greatly reduced thermal stresses in the coating, helping to prevent cracking occurring on cooling. This technique also enabled the coatings to be applied to carbon fibre reinforced polymers, which is of interest for potential use as rollers in the paper and print industries [67].

Spraying of recycled PET powder by both plasma and HVOF techniques has also been investigated [59]. The coating formed with plasma spray was found to be amorphous, but that formed by HVOF was crystalline. It was concluded by Lima, Takimi et al. [59] from substrate temperature measurements that this difference was due to the lower heat transferred to the coating and substrate by plasma than by HVOF. This meant the plasma sprayed coating cooled quickly, forming an amorphous coating, but the HVOF sprayed coating took longer to cool from a higher temperature, allowing the coating to crystallise [59]. Both techniques produced coatings free of porosity and cracks normal to the surface, but the plasma sprayed coating did exhibit some cracking at the polymer/substrate interface. Post heat treatment of the coatings was then investigated. where the coatings were heated well above the glass transition temperature then quenched. This proved to not only provide fully amorphous coatings with a smooth surface for both of the coating techniques, but also caused the cracks at the interface of the plasma sprayed coating to disappear. IR spectra of the coatings and initial PET showed no differences, indicating that there was no significant thermal degradation of the polymer at any stage of the processing [59]. Whilst post heat treatments such as annealing of coatings as performed by Lima et al. will not always be feasible in production situations, it proves the importance of being able to control the crystallinity of a coating to provide the desired coating properties.

2.4.7 Combustion spray of polymers

Combustion spraying of polymers has investigated the effects of surface pretreatment, coating adhesion and cohesion and coating crystallinity.

Surface pretreatment has been found to have a significant effect on adhesion of polymer coatings [53, 62, 69]. Degreasing of steel substrates was found to increase the adhesion of the polymer coatings, and grit-blasting to provide a rougher surface resulted in a further increase in coating adhesion due to mechanical interlocking [62, 69] and through the formation of a more active surface by removal of oxides on the substrate surface [53].

Coating adhesion was also found to be improved through pre-heating of the substrate. Pre-heating of the substrate is thought to improve adhesion through two mechanisms. Firstly pre-heating the substrate drives off condensates and adsorbates on the surface, reducing porosity in the coatings and increasing true contact area between the coating and the substrate [69]. Secondly pre-heating the substrate is thought to improve the flow of the splats on the substrate by reducing the cooling rate, again improving the true contact area and thus the adhesion [69]. Yan et al. found that preheating steel substrates to 140°C increased the peel strength of ethylene methacrylic acid copolymer coatings sprayed by flame spray from 1 N/mm² on room temperature substrates to 3.5 N/mm².

Corrosion resistance is an important factor in polymer coating quality. It has been shown that it is possible to form corrosion resistant polyamide-11 and fluoro-polymer coatings through the flame spray technique [70, 71]. Coating properties were found to improve with pre-heating of the substrates. McAndrew and Cere reported that flame sprayed polyamide-11 coupons exhibited good corrosion resistance but comparatively poor compared to fluidised bed dipped coupons when exposed to a salt fog spray chamber, with 3mm of encroachment after 30 days compared to 0.3mm for the fluidised bed dipped coupon. Adhesion of the coating exposed to the corrosive environment dropped by 30% over the 30 days [70]. Leivo et al. sprayed polyvinylidene fluoride (PVDF), ethylene chlorotrifluoroethylene (ECTFE), perfluoroalkoxy alkane (PFA) and fluorinated perfluoroethylenepropylene (FEP) by both flame and plasma spray techniques. Corrosion testing in salt fog, highly acidic and highly alkaline solutions is reported to have been performed, where all coatings are reported to have performed well, but no quantified data of the testing is reported. Coating cross sections were presented that showed dense poreless coatings, which is consistent with the reported corrosion results. It is noted that high density coatings require careful coating parameter optimisation, but no details of the optimisation were reported.

Crystallinity of flame sprayed PEEK coatings were found to be influenced by the cooling rate of the coatings [72]. It was found that the higher the crystallinity of a coating the lower its friction coefficient. It was also found that the coating with the highest crystallinity 30

had a decrease in wear rate for both increases of applied load and sliding speed [73]. A rapidly cooled flame sprayed PEEK coating was found to have 0% crystallinity and 5MPa of residual stress, whilst a slowly cooled coating had a 36% crystallinity and a residual stress of 48MPa [73]. The increase in crystallinity was also linked to a 30% decrease of the coefficient of friction for the coatings [73]. Zhang et al. reported that annealing of flame sprayed PEEK coatings results in a crystalline coating compared to the amorphous as coated condition, but whilst this resulted in an increase in Knoop hardness, annealing resulted in a qualitatively observed decrease in the adhesion of the coating to the substrate, determined by the amount of coating remaining on a substrate after peeling it off [74]. Coating adhesion was not quantified in this study, peel tests or similar should have been performed to provide quantified adhesion results.

2.4.8 Spray of polymers with filler particles

One of the primary aims of applying coatings is to improve the corrosion resistance or the wear resistance of the base material. To this end some research has been conducted into the thermal spraying of polymers with ceramic filler particles. Fillers not only provide excellent wear resistant coatings, they also help offset recrystallisation shrinkage and ensure coating cohesion. Filler particles absorb heat from the spray process and then release this heat on cooling to the polymer matrix. This release means that any unmelted particles may be melted by the heat retained by the filler particles.

One challenge is to achieve a good dispersion of filler throughout the polymer matrix. It has been found that in order to obtain a homogenously dispersed filler, the polymer needed to be injected at 45° to the plasma jet instead of perpendicularly. This configuration enabled the polymer particles to be entrained with the plasma and filler particles to provide even spread, whereas perpendicular orientation resulted in the polymer traversing the plasma plume, effectively depositing a layer of filler then a layer of polymer [75]. It has also been reported that reducing the diameter of the filler particles resulted in improved distribution of the filler particles in the coating [76].

Petrovicova et. al. sprayed nylon 11 by HVOF with both nano-sized silica and carbon black filler particles as blended powders [76, 77]. Alteration of the surface chemistry of the silica particles by silanation produced hydrophilic and hydrophobic silica, which affected the morphology and microstructure of the coatings. The hydrophobic silica with carbon black filler particles produced higher crystallinities than the hydrophilic silica. Larger diameter feed particles also gave a higher coating crystallinity.

Filler particles are primarily used to improve the wear resistance of polymer coatings. Petrovicova et al. found that scratch and sliding wear resistance were optimised with a nominal composition of 15 vol.% filler, resulting in a 35% increase in scratch resistance and a 67% increase in wear resistance compared to a pure polymer coating [77]. Additionally it was found that the rate of transmission of water decreased by up to 50% for coatings with the filler particles present [77]. In another study MDPE with an alumina filler was found to have wear properties approaching those of ultra high molecular weight polyethylene, one of the most abrasion resistant polymers. This resistance was due to the alumina filler particles not being worn away, but instead gradually being pulled out of the MDPE matrix [75].

2.5 Impact and spreading of single splats during thermal spray

The events that take place when a thermally sprayed particle impacts with a substrate or a previous layer of splats have a huge effect on the structure and properties of thermally sprayed coatings. However, these events are poorly understood, although much research has been performed, especially in the last decade, trying to understand the events that occur at and just after impact [57, 58, 60, 61, 65, 78-88]. Splat properties that are affected by the conditions on impact include splat shape, localised substrate melting, porosity, crystallinity, residual stresses and splat-substrate or splat-splat contact area, amongst others.

The factors involved in the impact and spreading of particles in thermal spray are numerous and include both particle and substrate variables. The particle variables include the state of the particle, whether it is molten, semi-molten or solid, the temperature profile through the particle, the velocity of the particle, and the angle with which the particle impacts the substrate. Substrate variables include the temperature of the substrate, the roughness of the substrate, the presence of any adsorbates or condensates on the substrate surface, and the quality of the contact between the splat and the substrate.

Madejski was one of the first to investigate this area when he looked at plasma sprayed alumina splats, and compared these to macro sized lead splats on aluminium [78]. Madejski reached the conclusion that modelling of the process was significantly complicated by the fact that splats start solidifying before they finish spreading. A very simplistic model assuming splats were cylinders was the result of his work, but it was really the first foray into understanding the science of particle impact.

Much of the initial work investigating single splats revolved around the splashing phenomenon. It was found that under certain conditions single particles impacting a substrate would leave disc or pancake splats, whilst sometimes fingered or flower shaped splats would form [57, 58, 88]. Fingered splats were considered to be the result of instable flow in the particle/splat upon impact. The reason for the flow instability was not agreed upon, but the probable causes were thought to be instability due to solidification of the splat before spreading was completed, disruption of the flow due to surface irregularities, and disruption of the flow due to degassing of greases and other adsorbates [57, 58, 61, 88]. This was investigated both through observation of experimental results and through mathematical modelling of the processes that govern splat formation [57, 58, 88].

Many factors need to be considered when trying to understand the processes occurring during the impact of a splat. This is complicated by the time scales of the processes as well, splat flattening typically only takes 1 to 5 microseconds, solidification typically 3-10 microseconds, formation of a layer of splats generally takes hundreds to thousands of microseconds and time between passes can vary from seconds to hours [61]. These timescales make imaging and recording splat impacts very difficult, but it has recently been achieved by Cedelle et al. [81, 82, 87]. Initial results indicate that fingered splats actually spread over the entire area of the fingers, then break up, with only the fingers remaining adhered to the substrate [81, 82]. This work observes thermally sprayed particles, so provides a better picture than work looking at scaled particles in a non-thermal spray system.

Fukumoto et al. reported work in which free falling droplet experiments were studied. The droplets had similar Reynolds (Re) and Weber (We) numbers as are found in thermal spray to make comparisons between thermal spray splats possible. Reynolds number is a non-dimensional number that provides the ratio of turbulent flow to laminar flow in a liquid. The Weber number is used to investigate the interface between two fluids and presents the ration of inertial force to the surface tension force. Splats were examined and the percentage of splats that were disc shaped and the number that were splashed were recorded, variables that were altered were the substrate temperature and the velocity of impact [79]. It was concluded from this work that splat cooling rate was dependent on the substrate temperature, a room temperature substrate resulted in a high driving force for solidification so solidification started before spreading was complete, resulting in unstable flow of the splat and hence splashing. A unique porous microstructure was also noted on the bottom of splats formed on room temperature

substrates [79]. Fukumoto et al. then compared thermal sprayed splats with free falling droplet experiments. The materials sprayed and deposited were Ni, Al, and Fe, and parameters investigated included substrate temperature, particle velocity, particle temperature and spray distance. From the experimental results a splashing parameter K was calculated, and the transition temperature of substrates where more than 50% of splats were disc shaped evaluated. The particle temperature and velocity were measured with the use of a DPV-2000 system from Tecnar [57]. The results showed that for all three metals sprayed (Cu, Ni, and Fe) the particles were molten in flight and that velocity decreased with spray distance beyond 50mm. As the temperature of a substrate is increased the number of disc splats increases, Fukumoto et al. defined the temperature at which 50% disc splats occur as the transition temperature T_t. They also introduced a modified flattening criterion which takes into account substrate temperature, K_f, which builds on the Sommerfeld flattening criterion K [80].

Sampath and Jiang further investigated the splashing and spreading of single splats. They noted the narrow temperature range $(100^{\circ}C - 400^{\circ}C)$ of the transition temperatures for different substrates compared with the wide range in the melting points of the particles impacting ($600^{\circ}C - 2600^{\circ}C$). Investigation of splat cooling rate led them to conclude that although solidification of splats before flattening is complete may partly lead to splashing, condensates and adsorbates on the surface may also play a significant role in the splashing phenomenon [58]. Fukumoto et al. and Sampath and Jiang investigated a range of powders, including metals and ceramics, sprayed onto a variety of substrates, including polished metal, glass and ceramic. However, all the spraying was performed with plasma systems. The use of plasma systems enabled the metal and ceramic particles to be heated to a fully molten state upon impact. No work was performed where spray conditions were constrained such that the metal or ceramic particles were solid or had a solid core upon impact [57, 58, 79, 89], such as is encountered in polymer thermal spraying.

Two papers have been published investigating skewness (Sk) as a roughness parameter to explain the spreading and splashing phenomena during thermal spray. In the first, Cedelle et al. [81] investigated millimetre and micrometre particles spreading on polished surfaces, with and without thermal treatment. They reported a positive change in Sk on $1\mu m$ square sample areas after thermal treatment of the surface had been performed. This positive change in Sk also corresponded to a change from splashed splats to disc splats and the cooling rate of splats. The spreading time on preheated substrates was found to be double that of splats on room temperature substrates, and cooling rates of

the splats similarly doubled [81]. Fukumoto et al. also investigated Sk on the nanometre scale but only for thermally sprayed particles. This work was in agreement with the work by Cedelle et al. and went further by investigating the change in surface after heating. It was found that similar numbers of disc splats were obtained for the 24 hours following preheating, but after that the fraction of disc splats decreased until after 60 hours less than 30% of splats were disc splats. This decrease did not, however, correspond to a change in Sk, and was thought to be linked to the accumulation of adsorbates and condensates on the substrate surface. By spraying onto gold substrates, with and without preheating, the effect of surface chemistry of the oxide layer was discounted, as gold does not oxidise in these conditions [90].

Due to the inaccuracies of modelling one group has focussed on imaging splat spreading. Mehdizadeh et al. devised a system combining CCD camera, long distance microscope, pulse laser, in flight particle detector and associated electronics that captured images of splats as they were spreading for the first time. The resulting images for the first time revealed what was actually occurring to splats upon impact with a substrate. The images revealed that soon after impact splats spread to their maximum diameter in one piece, but then break up as they cool and shrink, with only the centre of the impact and some fingers remaining adhered to the substrate, with the rest of the material not remaining deposited [88]. Further work by members of this group on room temperature and heated substrates has revealed that splats impacting heated substrates have a maximum diameter about one third that of splats impacting room temperature substrates. It was also found that heated glass substrates had a thermal contact resistance two orders of magnitude lower than for room temperatures substrates. This was predicted to have been caused by an insulating gas barrier between portions of the splat and substrate occurring at the room temperature condition [87]. The insulating gas layer was not investigated, but it is possible that it was due to desorption of water from the substrate surface due to thermal energy transfer from thermal spray torch and particle. As with the majority of single splat research, glass substrates were used in these experiments, with significantly different thermal and surface chemistry properties than metal substrates typically coated in industry.

Much work has also been done on modelling the process of flattening of thermally sprayed particles. In 1998, Zhang published a two dimensional numerical model and an analytical model of splat deposition that focussed on Re and We numbers of the particle and on ξ_m , the flattening ratio as defined by Madejski [78]. Zhang found his two models correlated well with each other and made improvements over early work by taking into

account particle solidification and heat transfer between substrate and particle [84]. In 2001 Zhang et al. published a volume of fluids model and compared the results of the model with single splats of molybdenum impacting molybdenum, mild steel and glass substrates. Results of this study found a definite correlation between substrate and particle temperature and the degree of splashing of splats. The results also suggested localised melting of the substrates occurred in some instances and that this greatly affected the adhesion of splats [83].

In 2002 Pasandideh-Fard et al. published a three dimensional numerical free surface fluid flow model of the flattening of single splats and compared it to experimental results of plasma sprayed Ni on polished stainless steel [85]. Their model took into account fluid flow, heat transfer and solidification. The model showed, if spreading was completed before solidification started no splashing occurred, but that to achieve this case the thermal contact resistance between substrate and splat had to be increased by an order of magnitude. It was also found that at a substrate temperature of 300°C the model predicted splashing, but heating the substrate to 400°C caused the model to predict the formation of disc splats. It was also experimentally found that the oxide layer which builds up on substrate heating increases the thermal contact resistance [85].

Li et al. provided a further numerical model that helped to explain a phenomenon noticed in microscopy of molybdenum splats on stainless steel, brass and aluminium where the splats resembled tectonic plates that had drifted apart from one another [86]. The conclusion reached was that the substrate was melting from the heat from the particle and kinetic energy of impact, and the splat was solidifying on a liquid layer of substrate, which allowed parts of the splat to drift apart, resembling tectonic plates or flowers.

The above models all shine light on the mechanisms that govern the spreading and splashing of single splats upon impact. Whilst no model will give all the answers they do show the importance of substrate temperature on the rate of solidification and the effect this can have on splat shape. This work has limited application to the field of polymer thermal spray and combustion spray processes, but does provide many insights that can be built on in the high velocity spraying of polymers. Polymers bring the problems of low thermal conductivity and viscous centres, and will be impacting at particle velocities of between 500ms⁻¹ to 700ms⁻¹ for HVAF spray compared to 200ms⁻¹ to 400ms⁻¹ as experienced in plasma spray.

All the above models focussed on metals sprayed by plasma systems. Ivosevic et al. have developed a model for nylon 11 sprayed by HVOF and compared the model with experimental results [60]. A volume of fluid three dimensional model was formed and compared to experimental results of zinc and nylon splats deposited on cold substrates to evaluate the differences between the sprayed materials. It was found that the significantly different physical and thermal properties (such as viscosity, conductivity, density) resulted in different splat morphologies for particles just above their respective melting points. The zinc particles resulted in a thin splashed splat, whilst the nylon particles resulted in a thicker disc shaped splat [60]. Refinements of the model in 2006 included the addition of a model of the HVOF torch and flame so that particle heating in the flame could be examined. The velocity and temperature profile through particles was then determined for particles of different diameters. Particles with diameters over 90µm were predicted to have solid cores upon impact which results in splats with a fried egg appearance. These predictions were validated under equivalent experimental conditions [56]. The effect of substrate roughness on the splatting behaviour of nylon particles was also examined. It was found that surfaces with Ra values equivalent to those generated in grit blasting significantly increased the degree of splashing and radial finger formation that the polymer particles exhibited upon impact. The model also revealed that the centre of the splats showed good intimate contact with the substrate due to the steep angle of flow to the surface, but that the edges of the splat where flow was more radial had markedly lower contact between splat and substrate [65]. Substrate heating above the melting point of nylon was found to result in hemispherical splats due to post deposition flow either as a result of surface tension, visco-elastic effects or residual stress in the "fried egg" structure seen on room temperature substrates [56, 60]. Models of the temperature of a polyimide splat after impact revealed that splats on a room temperature substrate cooled to the substrate temperature within 69µs, whilst splats on substrates heated to 320°C took 690µs to cool to the substrate temperature [64]. Bao et al. found that flame sprayed ultra high molecular weight polyethylene (UHMWPE) splats also exhibited a fried egg structure caused by a highly viscous core of the sprayed polymer particle that essentially remained solid upon impact [91].

2.6 PEEK

Poly aryl ether ether ketone (PEEK) is a polymer with a monomer unit as shown in Figure 2.16. The aryl rings with the stable links of ether and ketone groups give PEEK its chemical and physical characteristics, making it suitable for many engineering applications.



Figure 2.16 The monomer unit of PEEK.

PEEK is a high performance thermoplastic, that is, it is a thermoplastic with good resistance to both acidic and alkaline environments, is stable at relatively high operating temperatures (compared with most thermoplastics) and has good wear characteristics. One of the big advantages that PEEK exhibits over other polymers is its high melting point of 343°C [92].

PEEK is highly stable and suffers no chemical attack by water and steam, and also retains its mechanical strength and toughness at elevated temperatures. PEEK is able to be used in direct contact with food in the temperature range -196°C to 300°C [93]. PEEK also shows high resistance to a wide range of solvents, acids and alkalis, meaning that in the cleaning processes employed in food processing plants the PEEK will not suffer degradation during the high temperature alkali or acid cleaning regimes [92]. Characteristic properties of the PEEK 150PF supplied by Victrex are summarised in Table 2.2.

PEEK is a shear thinning polymer. This means that as the shear rate is increased the viscosity of PEEK decreases. This is significant as very high shear rates will occur during particle impact during thermal spraying, irrespective of whether the PEEK is sprayed by a plasma or HVAF system. At 350°C the viscosity of PEEK at a corrected shear rate of 4s⁻¹ was 1200 Pa.s, increasing the corrected shear rate to 125s⁻¹ resulted in a viscosity of only 500 Pa.s [94]. PEEK was also shown to be a visco-elastic polymer, with an elastic modulus on the order of 100000Pa at a shear rate of 1rad.s⁻¹ at 380°C. At the same temperature and shear rate, poly aryl ether sulfone had an elastic modulus of only 110Pa [95]. This data shows that the shear rate upon particle impact and visco-elastic forces within PEEK particles must be considered.

PEEK has a low coefficient of friction and good wear resistance, this makes it suitable for use in pumps for components such as rotors and bearings. The chemical resistance mentioned above increases the suitability of PEEK for use for components in pumps and other high pressure, wear sensitive situations [96].

Thermo-gravimetric analysis of PEEK as carried out by Lu et al. [97] found that there was no significant breakdown of the PEEK until 525°C, at which point significant thermal degradation started to occur. The coefficient of thermal expansion of PEEK was also measured with increasing temperature and was found to increase from 25μ m/m°C at ambient conditions to a maximum of 230μ m/m°C at 280°C. The coefficient rises significantly (as expected) above the T_g of 143°C [97].

Zhang et al. [98] investigated the mechanical properties of PEEK and PEEK composites. Their findings concluded that addition of short carbon fibres and lubricants including graphite and poly(tetrafluoroethylene) could significantly improve the wear resistance of PEEK, but this was at the cost of lowered toughness and strength. PEEK, however, remains a good matrix material for forming composites due to its high cohesive strength. PEEK is also being used for the formation of composites for use in hip replacements and similar in-vivo applications. Zhang et al. [99] found that carbon fibre - PEEK composites proved a suitable material for the compressive loading experienced by a hip stem, and that these properties were not affected by 7 months exposure at 95°C in a physiological saline solution.

Comparatively little work has been published on the thermal spraying of PEEK compared to some polymers such as nylon 11. Thermal spray however could potentially be an advantageous method for forming PEEK coatings that would enable the beneficial properties of PEEK to be harnessed in new and different industries.

Glass transition temperature (Tg)	143°C
Melting temperature (T _M)	343°C
Heat capacity (c _p)	2200 J.kg ⁻¹ .°C ⁻¹
Typical crystallinity	35%
Density: Amorphous	1260 kg.m ⁻³
Crystalline	1320 kg.m⁻³
Water absorption (equilb. at 23°C)	0.5%
Coefficient of thermal expansion:	
	$4.7 \times 10^{-5} \circ C^{-1}$
	4.7 ×10 0

Table 2.2 Characteristic properties of PEEK 150PF powder as supplied by Victrex.

2.7 Aims and methodology of this thesis

The thermal spray community recognises that substrate parameters have an influence on the properties of splats and coatings. However, most work has focussed on the effects of substrate roughness and heating on coating adhesion, with little thought to how surface chemistry affects adhesion or single splat properties. Whilst heating substrates has been shown to improve the adhesion of coatings, experiments investigating this phenomenon typically relied on splats deposited on glass substrates for ease of splat imaging, but which provide a significantly different chemistry than a metal substrate.

The aerospace and printing industries have long realised that chemical bonding across the metal polymer interface is critical for coating adhesion, and that to optimise bonding of polymers or organic coatings to aluminium substrates requires tailoring of the surface chemistry through chemical etches and/or pretreatments. This knowledge of the importance of chemical bonding between substrate and coating has application to the thermal spray industry, especially in improving the adhesion of thermally sprayed polymer coatings which typically have poor adhesion to metal substrates. The question arising from this is can a link be established between substrate surface chemistry and surface morphology and the measurable properties of polymer single splats (area, circularity) on metal substrates.

Little is known about what happens upon impact to polymer particles and similar high viscosity materials that are in a solid or semi-solid state upon impact. Work by Cedelle et al. [81, 82] and MacDonald et al. [87] is starting to offer insight into what is happening in the moments following impact of completely molten droplets, but does not yet extend to solid, semi-solid or visco-elastic materials such as polymers.

Polymers bring a new set of parameters to thermal spray with low particle thermal conductivity, low density, narrow thermal processing windows and visco-elastic flow properties upon impact. To generate adhesive coatings with low porosity without degrading the properties of the bulk polymer it is necessary to have a holistic understanding of the thermal spray system, from spray torch and particles, to the chemistry and morphology of the substrates being coated.

To attempt to find substrate parameters that will produce PEEK single splats of optimised parameters, that could translate into coatings of high adhesion and low porosity, it is

necessary to understand the influence that substrate chemistry and morphology have on PEEK single splats.

To address the lack of knowledge about the substrate surface chemistry, roughness and temperature on the properties of polymer single splats, this study used the following approach.

Aluminium was selected as a substrate as there is a significant knowledge base of its surface properties, and the chemistry of the surface oxide layer can be readily changed through chemical and thermal treatments. The effects of the chemical and thermal treatments on the surface chemistry were analysed by x-ray photo-electron spectroscopy. Thus the surface chemistries of the substrates on which single splats were deposited were known. Surface roughness and morphology of the surfaces were quantified with both scanning electron microscopy and atomic force microscopy.

Single splats were deposited using two separate systems, a Sulzer Metco 7MB plasma system and a Browning Aerospray 150 HVAF system. Single splats were deposited on room temperature substrates of differing surface pretreatments, and on substrates with the same pretreatments held at 323°C. Splats were also deposited on substrates with a polished surface at incremental temperatures up to 363°C.

By completing the above trials it enabled the following:

- Comparison of single splats on substrates of different surface chemistries at 23°C
- Comparison of single splats on substrates of different surface chemistries at 323°C
- Evaluation of the effect of thermal treatment on substrate chemistry and morphology
- Evaluation of the effect of thermal treatment of surfaces on single splat properties
- Comparison of single splats on substrates of the same pretreatment at 23°C and 323°C
- Evaluation of the effect of surface roughness on the properties of single splats
- Evaluation of the effect of surface temperature of a polished substrate on single splats
- Evaluation of the effect of different thermal spray processes on single splat properties
- Investigation into the effect the glass transition temperature may have on polymer single splats.

3 Experimental Methods

3.1 Substrate selection

Aluminium alloys 5005 and 5052 were decided upon as the substrates to be used due to experience in use of these alloys, and due to their relatively common use in industry. Using a high purity aluminium would have reduced the number of variables, such as surface precipitates, but it is far more common to employ aluminium alloys with up to 5% alloying elements in industrial situations, making the results gathered in this work more applicable to industry. The nominal compositions of AA5005 and AA5052 can be found in Table 3.1.

Whilst initial surface chemistry and spraying investigations were performed on AA5005, all spray results reported were deposited on AA5052 substrates. The surface chemistry work performed on AA5005 substrates was all repeated on AA5052 substrates and reported. The greater magnesium content of AA5052 had an effect on the surface chemistry of thermally treated substrates, as is discussed further in section 4.1.4.

3.2 Surface preparation

To evaluate the effect of the pretreatments on the surface chemistry and morphology on the aluminium surface a known initial condition was required. So that changes to morphology could be evaluated, the initial condition decided upon was a highly polished surface.

Initial surface chemistry and thermal spraying was performed on AA5005. Due to AA5005 being unavailable in polished sheets, AA5052 was selected as the substrate of interest. This removed the variation introduced by manual polishing of substrates and provided a more consistent substrate condition.

	Si	Fe	Cu	Mn	Mg	Cr	AI
5005	0.30	0.7	0.20	0.20	0.50-1.1	0.10	Balance
5052	0.25	0.40	0.10	0.10	2.2-2.8	0.15-0.35	Balance

Table 3.1 Nominal composition of AA5005 and AA5052 (mass %).

All substrates were stored in a desiccator with fresh desiccant between the various pretreatment steps and spraying. Substrates were always analysed and sprayed within two days of pretreatment preparation.

3.2.1 Polishing and degreasing

This step was common to all AA5005 samples. The samples were cut into various size square coupons from 7mm to 20mm to suit the various instruments with which they were to be analysed. The coupons were mounted on brass holders with a hot melt wax, and the brass holders were placed in a holder for attachment to a Struers Abramin (Westlake, OH, USA) metallographic grinding and polishing machine. The coupons were then surfaced by 220 grit silicon carbide paper. After surfacing they were ground with a 15 μ m diamond suspension, then polished with 6 μ m and 3 μ m suspensions of diamond, before being finished with a 0.4 μ m suspension of silicon dioxide. Between each of the stages the samples were washed with detergent and tap water, then dried with alcohol and hot air. This process left the samples with a mirror like finish.

Samples were degreased by placing them in a beaker containing acetone in an ultrasonic bath for a period of 10 minutes. This removed any vestiges of rolling oil or grease and also removed any remaining hot melt wax from the polishing stage. As AA5052 was purchased as pre-polished sheets, polishing was not required. Degreasing was performed by wiping the polished surface with a lint free tissue soaked in acetone after the protective backing had been removed. Wiping with acetone removed any adhesives remaining from the protective backing.

3.2.2 Etching

Four different etchants were initially trialled, FPL, P2, AcidBrite and P3 Almeco 29. The FPL etch is commonly used in industry as a pretreatment for aluminium surfaces before the application of paint or adhesives [9]. The P2 etch is a proposed replacement for FPL, trying to achieve the same surfaces but without the use of harmful Cr^{6+} ions which are present in the FPL etch. Both FPL and P2 are based on sulphuric acid.

AcidBrite is a commercial etch based on sulphuric and hydrofluoric acids. P3 Almeco 29 is a commercial alkaline etchant, and like AcidBrite was sourced from Henkel NZ Ltd (Auckland, New Zealand). Upon completion of etching all samples were removed from the etchant, washed with distilled water then dried with hot air. Compositions of the etchants can be found in Table 3.2. After XPS analysis of the generated surface chemistries it was decided to continue with only the AcidBrite etchant from Henkel.

Table 3.2 Etchant compositions.

FPL [9]	P2 [9]	AcidBrite [100]	P3 Almeco 29
			[101]
140.1g (76.2 mL)	185.0g of 98% H ₂ SO ₄	10% by mass H ₂ SO ₄	Borax, alkaline
of 98% H ₂ SO ₄			salts, phosphates
14.0g of Na ₂ Cr ₂ O ₇	75.0g Fe ₂ (SO ₄) ₃	15% by mass HF	and surfactants
1.1g of CuSO ₄	deionised water to	<10% by mass each of	Between 10% and
	0.500L	NH_4F_2 , inhibitors and	60% by mass for
		surfactants	each component
423mL of distilled		Mixed 3% vol/vol with	45g/L in distilled
water		distilled water	water

3.2.3 Boehmitising

Coupons were boehmitised by immersing the coupons in boiling distilled water. These coupons were removed from the boiling water after 30 minutes and patted dry with paper towels. Boehmitising is a hygro-thermal treatment of aluminium that forms a layer of boehmite, a meta-stable oxy-hydroxide of aluminium. A detailed explanation of the surface chemistry of aluminium and its oxides is presented in section 2.1.

3.2.4 Thermal oxidation

Sets of coupons that had been polished, boehmitised and etched were thermally oxidised at 350°C. The coupons were stored in a desiccator after their first treatment, then placed immediately into a cold furnace, and the temperature set for 350°C. The temperature then increased to 350°C over a 10 minutes period. The samples were left to "soak" for a further 80 minutes once the oven had reached 350°C.

3.3 Surface characterisation techniques

3.3.1 Atomic force microscopy

Atomic force microscopy is an analysis technique that can be used to measure topography and quantify surface roughness on the nanometre to micrometer scale. In this work a Digital Instruments NanoScope IIIa AFM (Veeco Instruments Inc. Plainview, NY, USA) was used to analyse surface roughness of substrates. It differs from SEM as instead of rastering an electron beam across the surface a fine silicon nitride (or similar) tip 2 to 3 microns long and approximately 100Å in diameter is rastered across the



Figure 3.1 Van der Waals forces relationship with distance, especially for the separation between AFM tip and sample, reproduced from [102].

surface, much like a phonograph needle. The tip is formed on the end of a cantilever 100 to 200 μ m long. Forces between the tip and the sample surface cause deflections of the cantilever. Tip position is commonly recorded by shining a laser onto the mirror-like back of the tip and reflecting the beam onto a position sensitive photo diode, allowing tip movements to be electronically recorded. Vertical height resolution is normally sub-angstrom as sensitivity can be altered by varying the ratio of tip to photodiode path length to the length of the cantilever [102].

Several forces affect the cantilever deflection, the most important of which are Van der Waals forces. These are short range forces that are repulsive at very close range and attractive further away as shown in Figure 3.1. Another important force is that due to capillary action. A thin water film on the sample surface can pull the tip towards the sample, typically with a force of about 10⁻⁸ N. The capillary force acts to keep the tip in contact with the surface. The final force present is that of the cantilever itself and is proportional to the cantilever deflection and the spring constant of the cantilever.

There are two main modes of operation of atomic force microscopy, contact and non contact. Contact AFM includes constant height and constant force microscopy. In constant height mode the vertical variation in the tip and cantilever is directly translated into topographical data. In constant force mode the cantilever deflection is returned through a feedback control circuit to keep the cantilever deflection constant. The image is then generated from the movements of the scanner to keep the deflection constant. The different modes have different applications, constant height mode is suited to making

atomic resolution images where there is little vertical variation, it is also used for collecting real time images of changing surfaces. Constant force is limited in scan speed by the speed of the feedback circuitry. It is used predominantly in AFM measurements as it exerts low forces on the sample causing less damage [102]. Tapping mode AFM involves the cantilever being oscillated near its resonant frequency (between 100kHz and 400kHz) through an amplitude of tens to hundreds of angstroms. The high separations used in non-contact mode result in small forces (about 10⁻¹² N) which are hard to measure, however, little contact between sample and tip means no damage is done, and makes it suitable for soft samples.

To study the effect of etchants on the surface morphology of aluminium a known surface condition first had to be prepared so all samples had the same starting point. This was initially achieved on AA5005 by grinding and polishing the 7mm square samples with sequentially finer diamond suspensions, finishing with a suspension of $0.4\mu m$ SiO₂ resulting in a mirror like finish. The manual polishing process was avoided when the AA5052 alloy was switched to as it became possible to source pre-polished aluminium. All aluminium samples were degreased then treated so as to form the six surfaces of interest, B, BT, E, ET, P and PT. These surfaces are defined and the treatments explained in section 4.1.4.

AFM was used to generate surface profiles of the surfaces and calculate the Ra values for those surfaces. The method for calculating surface roughness values is described in section 2.4.4. For each surface four squares of 50µm to a side were evaluated, and the results averaged. To get an accurate picture of the surface structure, the above samples were then imaged by SEM.

3.3.2 Scanning electron microscopy

Scanning electron microscopy provides images of surfaces at high magnification. The advantage of SEM is that it has a large depth of focus, which allows viewing of three dimensional aspects of samples at high resolution.

SEM is carried out under high vacuum because the electron beam used to generate the images would become scattered and weak if gas molecules were present in the specimen chamber. By maintaining a high vacuum the low energy secondary electrons used for imaging are able to be detected. As with x-ray photo-electron spectroscopy (XPS), specimens must be vacuum compatible.



Figure 3.2 Schematic of the interaction of electrons with a sample in an SEM. I is the incident electron beam, SE's are the secondary electrons.

SEM works by rastering an electron beam across the specimen generating a range of signals. The electron beam is generated by an electron source then accelerated towards the sample at a range of different voltages depending on the sample properties. The beam is focussed to a small spot, this spot defines the resolution to which the microscope is capable of resolving objects. When the electrons strike the surface they interact with a pear shaped volume below the surface, in which they suffer elastic and inelastic collisions, resulting in the release of back scattered electrons, secondary electrons, auger electrons and x-rays.

Secondary electrons that are generated provide information about the surface topography. They are generated through the entire interaction volume during inelastic collisions, but their low energies result in only those generated near the surface (about 5 nm) escaping without suffering inelastic collisions. Thus depending on the angle of the surface to the incident beam, and the resultant change in escape volume of the surface, the number of secondary electrons generated from the interaction volume differs, as shown schematically in Figure 3.2. This gives contrast to the picture, different slopes returning different intensities of secondary electrons. Shadowing of parts of the surface by projections that effectively block the path of the electron beam gives contrast and shading to images. Secondary electrons are attracted to an Everhart-Thornley detector by a charged grid where they are counted. The intensity of the secondary electrons from each point on the surface is then used to generate a grey-scale image of the surface.

The model of SEM used to analyse substrates and splats in this research was a FEI Quanta 200 FEG environmental SEM (Hillsboro, OR, USA). Experimental conditions varied, but predominantly an excitation voltage of 20kV was employed with a beam current of 200nA.

3.3.3 X-ray photoelectron spectroscopy

Two XPS instruments were used in this work, initially a Kratos XSAM 800, then a Kratos Axis DLD (Manchester, UK), a higher resolution instrument. All coupons were evaluated by wide scans and narrow scans of the O 1s, C 1s and Al 2p peaks.

For the Kratos XSAM 800 wide scans were conducted at 65kV, 1.0eV step size and two 2000ms sweeps. Narrow scans were conducted at 20kV, 0.1eV step size and 3000ms sweeps, the number of sweeps varying depending on the signal strength of the individual peaks. All scans were conducted with a Mg x-ray source.

For the Kratos Axis DLD wide scans were conducted at 160kV, 1eV step size. Narrow scans were conducted at 10kV and 0.1eV step sizes. All scans were conducted with a monochromatised Al x-ray source.

Due to charge build up brought about by the loss of photoelectrons from the surface some of the results suffer from charge shift. Charge shift was remedied by shifting all spectra such that the main C 1s peak was at 285.0eV, where it is generally agreed to be in the literature [19, 20, 38, 45]. The main C 1s peak is due to adventitious carbon that adheres to samples while they are exposed to ambient atmospheres and is due to the C-H bonds in long chain hydrocarbons. All binding energies are quoted after adjustment to a C 1s peak at 285.0eV.

The wide scan of each surface revealed the elements present on the surface of the aluminium coupons. To quantify the elemental composition of the surface the intensity of each elemental peak above the background level was recorded. These intensities were then normalised against their respective atomic sensitivity factors. This compensated for the different peak intensities of each element given an x-ray source of known wavelength. The percentages of the normalised intensities then equated to the percentages of each element present in the surface layer analysed by XPS (about 5nm deep).

Narrow scans of individual x-ray peaks reveals the oxidation state or states of the element that is being analysed. The oxidation states can then be used to determine the form in which the element is present, i.e. whether oxygen is present as an oxide, a hydroxide or as chemisorbed water, as described in section 2.3. To determine oxidation states it is often necessary to deconvolute the narrow scans.

Deconvolution is a mathematical process where a narrow scan is broken into component curves, each due to a different oxidation state. Four different software packages were evaluated for peak deconvolution, the two vision packages that were supplied with the two XPS, XPSPeak, a freeware XPS deconvolution package, and CasaXPS, a robust high end package that emulates and extends upon the vision packages that Kratos supply, with CasaXPS selected for final data analysis. An oxygen 1s narrow scan is shown in Figure 3.4, it was collected from a boehmitised aluminium surface. Spectra such as the O 1s scan shown in Figure 3.4 are deconvoluted with information from literature on the number of peaks, the peak positions and the full-width half maximum (FWHM) measurement expected of a given compound. This data allowed the two peaks of a boehmitic surface to be fitted, and the characteristic curve shape to be determined, a 70% Gaussian, 30% Lorentzian curve for this research. Curves are normally modelled mathematically as part Lorentzian function and part Gaussian function as demonstrated in Figure 3.5. The ratio of Lorentzian to Gaussian was determined from the O 1s spectra of the boehmitised surface due to its easy deconvolution into two equal components. With this information more complex O 1s spectra were able to be deconvoluted, an example of which, an AcidBrite etched aluminium 5052 surface is shown in Figure 3.6. Aluminium 5005 substrates were deconvoluted entirely in accordance to the work by Lopez et al. [45], with O 1s spectra fixed relative to the Al 2p peak positions. When substrates were changed to aluminium 5052, the more robust method of fixing the O 1s peak position to a known and referenced binding energy was used. The binding energy selected for fixing was that of Nylund and Olefjord, who accurately defined this position in their work [19].

When deconvolution of a spectrum is complete, the areas under each curve can be calculated. The fraction of the area under each curve compared to the total area under the O 1s spectrum then represents the percentage of the oxygen atoms that are in that oxidation state. Thus the amount of oxide, hydroxide and chemisorbed water present on a given aluminium surface can be determined from the different oxidation states of the oxygen atoms in each of the oxide, hydroxide and chemisorbed water functional groups.

Due to the thickness of the boehmitic layers, ion beam analysis techniques were used to evaluate oxide thickness and composition of B and BT samples. This analysis was performed by GNS Science. Ion beam techniques however were not suitable for P, PT, E or ET substrates (as defined in section 4.1.4) as it requires a minimum film thickness of 50nm. Two ion beam techniques were used in conjunction with each other, Rutherford backscattering spectroscopy (RBS) and elastic recoil detection analysis (ERDA).



Figure 3.3 Characteristic wide scans of two polished aluminium 5005 surfaces with chemical peaks as labelled.



Figure 3.4 Deconvoluted O 1s narrow scan of a boehmitised aluminium 5005 surface.





Figure 3.5 Normalised Gaussian and Lorentzian distributions, and a typical curve used in XPS curve fitting.



Figure 3.6 An O 1s narrow scan of an AcidBrite etched aluminium 5052 surface.

Rutherford backscattering is a widely used surface analysis technique in many branches of materials science. Basically a beam of energetic ions is directed onto the material under investigation. The ions scatter elastically from target atoms within the sample and are backscattered into a suitable detector, which counts the number of scattered particles and measures their energy [103]. The information contained in the scattered particles can be interpreted to give elemental composition of the sample, the distribution of elements within the sample and the sample thickness. Elemental depth profiles are usually measured with helium particles. ERDA was used here to measure the hydrogen content of the aluminium oxide layer. The experimental conditions used for the ion beam analysis are summarised in Table 3.3. A mylar film of 10 μ m thickness was attached in front of the ERDA detector to absorb all the scattered and recoiled atoms except hydrogen. The depth resolution is estimated to be around 50 nm at the sample surface by taking the FWHM of the H surface peak measured from a standard Si wafer [103]. Hydrogen implanted Si samples were used as calibration standards. Using these experimental parameters, the depth of analysis of hydrogen is approximately 800 nm.

	ERDA	RBS
lon beam:	⁴ He⁺	⁴ He⁺
Particle energy:	2.5 MeV	2.5 MeV
Total charge:	20 µC	5 µC
Sample tilt angle:	70°	0°
Detector angle:	30°	165°
Detector filter:	10 µm of Mylar	None
Detector collimator:	diameter = 1.5 mm	diameter = 1.0 mm
SBD detector area:	50 mm ²	50 mm ²

 Table 3.3 Ion beam analysis experimental conditions.

4 Surface Chemistry and Morphology of Aluminium

4.1 Surface chemistry

The surface chemistry and surface morphology of a substrate are two variables that have large potential to affect the spreading and adhesion of thermally sprayed splats. To characterise the surface chemistry of aluminium substrates XPS was performed, and surface morphology was evaluated by both AFM and SEM.

Aluminium surface chemistry can be altered by a variety or techniques, as explained in detail in section 2.1. Boehmitising, chemical etching, and thermal oxidation singly and in combination were used to alter the surface chemistry of aluminium in this study. These different treatments change the molecular composition of the surface layer of the aluminium and can therefore have an effect on the interaction between a splat and the aluminium substrate.

4.1.1 Surface composition of treated substrates

Seven different substrates were evaluated by XPS to determine the effect of various pretreatments on the surface chemistry of aluminium 5005, the seven substrates are listed in Table 4.1.

As discussed fully in section 2.1, the surface of aluminium can be comprised of many different components, including Al₂O₃, Al(OH)₃, AlOOH, and structural variants of these species. The results of the XPS wide scans of the sample surfaces are presented in Table 4.2. These results confirmed that chemical pretreatments predominantly work by modifying the properties of the surface oxide layer, rather than depositing or bonding additional chemicals to the surface of the coupons. All coupons had the expected adventitious carbon, oxygen and aluminium peaks independent of the preparation The trace fluorine present in most coupons was from adsorption from technique. fluoridated town supply water used in the polishing process. The sulphur present on the P2 and FPL coupons is believed to be sulphates adsorbed onto the surface from the sulphuric acid in the two etches. The nitrogen is believed to be present due to polymer cross-contamination of the acetone used in degreasing. Copper and zinc present on the polished coupon are believed to be contaminants from the polishing wheels despite best practise being adhered to. Silicon on the polished, and polished and degreased coupons was present as SiO₂, a remnant of the final polishing stage, whereas the silicon on the

Alm29 and AB coupons was present as organic silicones and was from the surfactants used in these two commercial etchants. Examples of the wide scans that generated the elemental compositions are presented in Figure 4.1.

	-	• •					
Surface	Al	Al acetone	AI	AI FPL	Al P2	Al	AI P3
treatment	polished	degreased	boehmitised	etched	etched	AcidBrite	Almeco
						etched	29 etched
Abbreviation	Р	DG	BWI	FPL	P2	AB	Alm29

 Table 4.1 Summary of the coupon pretreatments.



Figure 4.1 XPS wide scans of a polished (top) and an AcidBrite etched (bottom) aluminium 5005 substrate.

Atomic (Atomic Concentration (%)									
Peak	Ρ	DG	FPL	BWI	P2	Alm29	AB			
0 1s	46.5	39.9	44.9	37.4	48.6	45.1	42.7			
C 1s	24.8	33.2	33.3	47.1	28.3	28.9	25.5			
Al 2p	24.4	21.1	18.7	15.5	19.9	21.1	23.7			
S 2p	-	-	1.5		1.8	-	-			
F1s	0.3	0.6	1.4		1.4	0.7	5.1			
N 1s	-	1.6	0.2		-	-	-			
Si 2p	2.5	1.6	-		-	2.9	2.6			
Cu 2p	1.3	-		-			-			
Ca 2p	0.2	-		-		0.3	-			
Na 1s	-	2.1	-		-	1.1	0.4			
Zn 2p	0.2	-	-	-	-	-	-			

 Table 4.2 AA5005 coupon surface compositions following surface treatment.

4.1.2 Oxide layer composition of different etched surfaces

The oxide layer present on the surface of aluminium reacts with atmospheric moisture to form a variety of hydroxides and oxyhydroxides, as discussed in section 2.3. This results in three resolvable oxygen peaks when conducting XPS analysis, one due to an Al-OH bond, one due to the Al=O bond in AlOOH and one due to chemically adsorbed water [38]. Sulphate and silicon oxide contaminants have not been taken into account during fitting of the O 1s spectra, but the levels were too low to affect the fitting of peaks to the O 1s spectra.

As can be seen from Figure 4.2, the BWI samples had equal proportions of O:OH and no adsorbed water, indicating a pseudoboehmitic surface was formed, as expected. This result was used to define the peak widths and separation of the oxide and hydroxide peaks. The separation of the Al 2p oxide peak and the O 1s oxide peak was then measured for the BWI samples. This separation was then used to fit the O 1s oxide peak on subsequent samples, in accordance with the work of Lopez et al. [45], and is displayed on a wide scan in Figure 4.3. Using this as a basis, the chemisorbed water peak was defined on the FPL and P2 samples which were known to be Si free from the wide scans. Figure 4.4 shows that both the FPL and P2 etchants produced a high degree of chemisorbed water on the substrate surface, but with P2 samples having slightly more chemisorbed water. In contrast the P, DG and Alm29 samples had very low chemisorbed water. It is proposed that the degree of chemisorbed water is an indicator of the reactivity of the surface of the aluminium, where atmospheric moisture had very

quickly bonded to these active surfaces. By this argument, P2 and FPL treatments provided the most active surfaces, followed by AB, Alm29, DG and P, with BWI producing an inactive meta-stable surface. Most importantly it can be seen from Figure 4.4 that each pretreatment produced a substrate with a unique and distinguishable surface chemistry. All samples were placed in high vacuum immediately after preparation, ensuring minimum dehydration and change of the pre-treated substrates.



Figure 4.2 Deconvoluted XPS O 1s spectra from polished and degreased, boehmitised, and FPL etched aluminium 5005 substrates (from top to bottom).



Figure 4.3 Shown are the wide scan and O 1s narrow scan of a BWI substrate.



Figure 4.4 Summary of the oxygen peak spectra breakdown representing how much of the O 1s spectra was due to each of its component parts.

4.1.3 Surface acidity measurements

The binding energies of the O 1s (oxide) peaks to the Al 2p (oxide) peaks for the different surface pretreatments were plotted against each other, as displayed in Figure 4.5. The difference in binding energies was essentially constant, resulting in an approximately straight line of slope 1. The further to the right on this graph, the more acidic the surface is, the further to the left, the more basic the surface [45]. The acidic positions of FPL and P2 etched substrates, and the basic position of boehmitised substrates agreed well with



Figure 4.5 Oxygen 1s binding energies vs. Aluminium 2p binding energies. A distinct trend can be noticed, with acidity increasing as the BE increases.

Pretreatment	FPL	P2	BWI	DG	P	Alm29	AB
Mean thickness	6.1	7.1	>8.0	3.5	3.7	4.0	3.5
(nm)							
Range (nm)	5.2 - 6.8	6.0 - 8.0	-	3.4 - 3.6	3.2 - 4.1	3.9 - 4.1	3.5 - 3.5

Table 4.3 Thickness of oxide layers resulting from each pretreatment.

the findings of Lopez et al., but the large spread in the FPL and P2 data meant that this was of limited use in determining acidity. It did allow the selection of AcidBrite and boehmitising pretreatments, with relatively little scatter, and at separate ends of the substrate acidity scale of those pretreatments tested.

The large variation in oxide layer thicknesses resulted from charging of the substrates, which was believed to result in the spread of the acidity data. The thicknesses of the oxide layers are presented in Table 4.3. The thickness measurements are the mean of two values for all pretreatments except FPL etching, which is the mean of four values.

In summary, it has been shown that pretreatments of aluminium substrates did not deposit additional molecules on the surface, but instead altered the various forms of aluminium oxide on the surface, which can be analysed by XPS. Surface acidity was not able to be quantified through XPS, but two pretreatments, boehmitising and etching with AcidBrite, which produced substrates with significantly different acidities, were selected. The ability to alter the surface chemistry of aluminium through pretreatments meant that in conjunction with knowledge of chemical bonding between organic molecules and aluminium surfaces, a pretreatment which optimises adhesion and wettability of polymer splats during thermal spraying is possible.

4.1.4 Surface chemistry pretreatment, AA5052

The substrates were changed from AA5005 to AA5052 at this point, from this point forward all substrates discussed are AA5052 unless stated otherwise. After initial investigations of a range of chemical pretreatments, the six treatments summarised in Table 4.4, and fully explained in section 3.1, were selected for further investigation and thermal spraying. Boehmitising was selected as it produced a relatively basic aluminium oxy-hydroxide surface with a known chemistry and known bonding groups on the surface. Etching with AcidBrite was chosen as a pretreatment due to the consistent acidic surface it produced, significantly different to the boehmitised surface. AcidBrite also produced a rough surface for comparison to the polished surface, surface roughness of all the pretreatments sprayed are characterised in section 4.2. A polished and degreased surface was chosen to represent a control surface with an oxide layer formed in ambient air, with minimal roughness so as to evaluate the flow of a splat across a smooth surface. These three surfaces were all subjected to thermal oxidation to investigate the effects of surface roughness on splat morphology, based on the expectation that oxidation at 350°C would form a dehydrated oxide layer on all the pretreatments.

As can be seen from Table 4.5, all coupons had the expected adventitious carbon, oxygen and aluminium peaks independent of the preparation technique. The presence of magnesium was not surprising due to the bulk composition of AA5052, as shown in Table 3.1. The high concentration present in the ET and PT thermally treated samples was due to preferential oxidation of magnesium under thermal oxidation conditions, where the magnesium diffuses to the surface and oxidises [104]. The BT sample, however, showed no magnesium present on the surface, indicating that the boehmite layer was so thick that the magnesium did not have sufficient time to diffuse through it to the surface. The

Sample label	Boehmitised	Boehmitised and thermally oxidised	Etched	Etched and thermally oxidised	Polished	Polished and thermally oxidised
Sample	В	BT	E	ET	Р	PT
Reference						
Polished	Х	Х	Х	Х	Х	Х
Degreased	Х	Х	Х	Х	Х	Х
Boiled	Х	Х				
Etched with			Х	Х		
AcidBrite						
Thermal		Х		Х		Х
oxidation						
(1 hr, 350°C)						

 Table 4.4 Summary of the coupon pretreatments.

calcium peaks present on the ET and PT wide scans probably arose from contamination from the furnace, as does the Si on the ET sample. In the case of the P sample, the calcium was probably due to a little contamination during transport, as calcium is commonly associated with dirt and contamination in both SEM and XPS analysis. The fluorine peak present in the E and ET samples was from the hydrofluoric acid in the AcidBrite etchant used. The fluorine peak on the P and PT sample was from part of the polishing process, fluorine has a high affinity to bond to aluminium and can even be present due to exposure to fluoridated tap water. The B and BT samples probably had a small amount of fluorine present as did the P and PT samples, but the thick boehmite layer that formed on their surfaces formed above the fluorine and as such the photoelectrons from the fluorine did not escape the oxide layer as they were too deep. However, these results also showed that if the oxide layer was thin enough thermal treatment of AA5052 resulted in the diffusion of magnesium to the surface and its preferential oxidation. The magnesium present on E, ET, P and PT substrates was present in the form of either magnesium oxide (MgO) or MgAl₂O₄. Both of these forms of magnesium readily hydrate in the presence of water [27]. Stralin and Hjertberg also found that the presence of magnesium on an aluminium surface increased the rate of hydration of the surface through disrupting the Al₂O₃ layer and providing diffusion pathways for the hydroxide and hydrogen ions [27]. Hydration of the aluminium was found to improve bonding of both low density polyethylene and an ethylene-butyl acrylate copolymer to the substrate [27, 105-107]. Thus the presence of magnesium on the surface of these substrates will increase the hydration rate, and potentially improve adhesion of polymer splats.

	Atomic %								
Element	В	BT	E	ET	Р	PT			
O 1s	66.8	70.7	28.7	30.1	23.2	32.1			
C 1s	20.6	16.3	35.4	22.6	42.6	18.6			
Al 2p	12.6	13.0	33.2	23.1	26.0	9.6			
Mg 2s	0.0	0.0	0.9	17.6	6.7	29.0			
Ca 2p	0.0	0.0	0.0	4.0	0.9	9.7			
F 1s	0.0	0.0	1.7	0.3	0.7	1.0			
Si	0.0	0.0	0.0	2.3	0.0	0.0			

Table 4.5 Surface compositions due to each surface treatment.







4.1.5 Oxide layer composition and thickness of selected pretreatments

The change to AA5052 substrates necessitated further XPS to not only verify the elemental composition as reported above, but also to determine the effect of the pretreatments on the aluminium oxide species present on the substrate surfaces. The results for the six selected pretreatments on AA5052 are presented in Figure 4.7. Whereas the AA5005 substrates were prepared fresh and then immediately placed in high vacuum, the AA5052 substrates were prepared, then stored in a desiccator for a period of about 24 hours before being placed in the high vacuum of the XPS. This was the same procedure used for spraying substrates, where pretreatments were performed 24 hours before spraying, during which time they were stored in a desiccator, thus these results represent as accurately as possible the surface chemistries of the substrates as they were coated. Some differences existed between the surface chemistries of the AA5005 substrates and the AA5052 substrates. The primary distinction between the surface of AA5005 substrates and the ET and PT AA5052 substrates was the large magnesium peak on the AA5052 substrates, which formed as the result of diffusion of magnesium to the surface of the oxide layer during thermal treatment. The other significant difference was the contamination of the samples, AA5052 substrates showed very low levels of contamination, from the ceramics of the heat treatment ovens and fluoridated water. In comparison the AA5005 had a high degree of contamination from a variety of sources. The low level of contamination of the AA5052 substrates was due to lessons learned from preparation and treatment of the AA5005 substrates.



Figure 4.7 Summary of the oxygen peak spectra breakdown representing how much of the O 1s spectra was due to each of its component parts.

As can be seen from Figure 4.7, the BWI samples had essentially equal proportions of oxide and hydroxide on the surface, as was the case for the AA5005 substrates. Boehmitising of AA5052 resulted in some chemisorbed water on the surface which was not present on AA5005 substrates. The etched surface was significantly different to the AB substrate on AA5005, probably a result of storage in a dry environment as opposed to direct transfer to high vacuum. The polished surface showed no chemisorbed water on the AA5052 substrate, probably a result of the industrial polishing process, as compared to the wet polishing process followed for the AA5005 substrates. Although there were differences between the AA5005 and AA5052 substrate chemistries they still differ from one another significantly and provided variations in surface chemistry and morphology.

Analysis of the results displayed in Figure 4.7 show that the pseudoboehmite surface chemistry of the B sample was thermally stable, and the BT surface exhibited essentially the same surface chemistry. The presence of slightly more chemisorbed water was probably the result of thermal treatment partially "activating" the surface, effectively converting some boehmite to water, which then chemically adsorbed to the surface. Theoretically dehydration of a boehmitised surface should result in the formation of a layer of corundum [22]. However, the meta-stable nature of boehmite requires a significant degree of thermal energy and time to reach equilibrium. The results of this study, as shown in the surface chemistry results section, showed that heating to 350°C for 1 hour 30 minutes was not hot enough, nor long enough for the formation of corundum. The increase in the amount of chemisorbed water on the surface of BT substrates, however, showed that thermal treatment resulted in the formation of some of the transition phases, as discussed fully in section 2.3. The change on thermal treatment for the E surface to ET was of particular note, a surface which started off with a high hydroxide content (note: this was not a boehmitic surface, as boehmite only forms under hydrothermal treatment) and the ET surface having much of the hydroxide oxidised to oxide, but with no growth of the oxide layer, as shown in Table 4.7. It should also be noted that thermal oxidation of the etched surface resulted in a significant presence of magnesium oxide on the surface. The only effect of thermal treatment on the surface chemistry of a P surface was the preferential diffusion of magnesium to the surface and its subsequent oxidation, resulting in a high magnesium content, similar to the etched and thermally treated surface. The E and B surfaces appeared to have similar ratios of oxide, hydroxide and chemisorbed water on the surface, however, from the processing conditions it is known that the boehmitic surface would have a layer of boehmite which forms at 100°C when aluminium is exposed to water, whilst the etched surface, prepared
at ambient temperature of 20°C, could not be boehmitic, and must therefore be composed of $AI(OH)_3$ and amorphous AI_2O_3 with a little chemisorbed water. This was a difference that XPS alone could not reveal. Due to this, the surface chemistry of the BT surface could not be known with absolute certainty, but it was probable that the oxide layer was a combination of a boehmite, $AI(OH)_3$ and AI_2O_3 .

The different surface compositions represented in Figure 4.7 were evidence of the different chemical compositions of surfaces given differing pretreatments. The change in hydroxide concentration on the etched surfaces with thermal treatment, the different surface chemistries and morphologies of boehmitised and etched surfaces, the chemical differences between polished and boehmitised surfaces, and the similar chemistries yet differing morphologies of ET and PT surfaces allowed interpretation of the shape and spreading of PEEK splats with clearly defined knowledge of the properties of that surface and comparison surfaces. Particularly, the similarity in chemistry of the ET, P, and PT surfaces shown in Figure 4.7 were beneficial in separating the effects of surface morphology from those of surface chemistry on the properties of single PEEK splats.

Due to the limitations of XPS for analysis of B and BT substrates, they were analysed by two ion beam techniques, Rutherford backscattering spectroscopy (RBS) and elastic recoil detection analysis (ERDA). The results from RBS and ERDA are presented in Table 4.6. This shows that both B and BT substrates had an oxide layer 226nm thick, with a diffusion zone into the base metal which was 66nm thick. The compositions of the two oxide layers were essentially identical, showing that thermal treatment had no effect on the composition of the surface chemistry of the BT substrates. The ratio of elements present in the oxide layer was in accordance with the expected boehmitic surface, confirming the indication of the XPS results.

	Layer #	Sub-layer compositions			Estimated
					thickness
		Al	0	Н	nm
Boiled (B)	1	29%	52%	20%	140
	2	29%	52%	20%	86
	3	61%	24%	15%	66
Boiled and thermally treated (BT)	1	29%	52%	20%	140
	2	31%	55%	15%	86
	3	61%	24%	15%	66

Table 4.6 Summary of ion beam analysis results for B and BT substrate surface chemistry.

4.2 Surface morphology

Upon surface modification the samples were placed on atomic force microscopy (AFM) sample stubs and the surface morphology imaged by AFM. A representative area was selected, and four sub samples of 50µm squares were taken to evaluate the surface roughness.

As can be seen from Figure 4.8 and Figure 4.9, thermal treatment of the surfaces had no significant effect on morphology of the surface, which was confirmed by the Ra values presented in Table 4.7. The polished and boehmitised surfaces are both very smooth, with boehmitising only resulting in a slight increase in roughness of the surface. In contrast, etched substrates had a very rough surface with significant potential for mechanical keying to the surface for increased adhesion of polymer splats.

The oxide thicknesses for the E, ET, P and PT surfaces were determined by XPS, by the method outlined in section 2.3. The photo-electrons measured in XPS could not penetrate the thick oxide layers of the B and BT substrates, meaning a comparison of the intensity of the Al 2p metal peak and the Al 2p oxide peak was not possible. The oxide thickness of the B and BT layers were instead determined through the use of two ion beam analysis techniques, Rutherford backscattering spectroscopy (RBS) and elastic recoil detection analysis (ERDA).

The E, ET, P and PT samples had very similar oxide layer thicknesses, as can be seen from Table 4.7, and whilst thermal oxidation increased the thickness of the P oxide layer, it had no effect on the E oxide layer thickness, suggesting that etching stabilised the oxide layer compared to a polished substrate. There was no change in oxide layer thickness of a boehmitised substrate with thermal treatment. Despite the relatively constant oxide layer thicknesses with thermal treatment, as shown in the previous section, oxide layer composition changed significantly with thermal treatment. It was important to know the thickness of the oxide layer as heat will be conducted through the

Table 4.7 Thickness and surface roughness of the oxide layers resulting from the different pretreatments.

	В	BT	E	ET	Р	PT
Oxide layer thickness (nm)	226	226	4.0	4.1	3.4	6.5
Ra (nm)	34 ± 5	18 ± 5	253 ± 20	254 ± 20	12 ± 3	12 ± 3

oxide layer away from impacting splats, the thicker the insulating oxide layer, the more slowly a splat will cool.

Analysis of substrate surfaces by XPS, AFM and SEM provided an accurate picture of the chemical and morphological states resulting from the six pretreatments selected for preparing AA5052 substrates for thermal spraying. In terms of surface chemistry, it has been shown that B, E and P substrates all had significantly different surface chemistry, with differing amounts of oxide, hydroxide and chemisorbed water on the surface.

Surface chemistry of the E and P surfaces altered significantly with thermal treatment, leaving the surface chemistry of ET distinct from E, and PT distinct from P. XPS was inadequate to evaluate the changes between B and BT, but RBS and ERDA analysis revealed no difference between B and BT surface chemistries. ET and PT substrates had very similar surface chemistries, which differed significantly compared to that of the BT substrates. The 6 pretreatments thus resulted in 4 distinct surface chemistries, summarised in Table 4.8 ([P], [E], [B/BT], [ET/PT]), where the fraction of oxide, hydroxide, chemisorbed water and boehmite present on a surface are known. Similarly the oxide thickness and surface morphology of each substrate are known, with essentially two oxide thicknesses ([B/BT], [E], [ET], [P/PT]) and 3 roughnesses ([B/BT], [E/ET], [P/PT]).

With surface chemistry, roughness and oxide layer thickness (resistance of heat conduction away from splats) all expected to play an influence on the spreading, wetting and splat morphology of polymer splats, the knowledge of these properties enabled the correlation of splat properties with substrate conditions.

Pretreatment	Features	Oxide thickness
Р	Roughly 65% Al_2O_3 , 35% $Al(OH)_3$, no magnesium.	3.4 nm
E	Roughly 60% Al(OH) ₃ , 40% Al ₂ O ₃ – <u>not</u> boehmitic.	4.0 nm
B and BT	Boehmitic surface, similar chemisorbed water.	226 nm
ET and PT	Roughly 65% Al ₂ O ₃ , 35% Al(OH) ₃ , <u>high</u>	~ 4.5 nm
	magnesium.	

Table 4.8	Significant features of the surface chemistry of the different pretreated
substrate	S.



Figure 4.8 AFM images of the 6 pretreated surfaces. Images are of a 100 μ m sample square, with a scale of 2 μ m in the z axis.



Figure 4.9 SEM images of the 6 pretreated surfaces. Images are ~40µm square.

5 Single Splat Experimental Methodology

5.1 Thermal spray torches

Two thermal spray torches have been used in this work, an HVAF Browning Aerospray 150 (Browning Thermal Systems Inc. Enfield, NH, USA), and a Sulzer Metco 7MB (Sulzer Metco, Winterthur, Switzerland). The HVAF Browning Aerospray 150 combusts kerosene and compressed air. The powder feed was radial to the gas jet and was fed at the entry of the spray nozzle. The Sulzer Metco 7MB is a plasma torch where heat was provided by a nitrogen plasma generated by a dc electric arc between two electrodes. Particles were radially fed into the plasma plume, where they were heated and propelled onto the substrate. Full descriptions of the processes can be found in section 2.4.1.



Figure 5.1 Left, SEM image of PEEK particles. Right, cumulative particle size distribution of PEEK powder by particle number percentage.

5.2 PEEK powder

The PEEK powder sprayed was grade 150PF, supplied by Victrex Plc. (Lancashire, UK). The 150 refers to the low viscosity of the PEEK, PF represents that it is supplied in fine powder form. Nominal particle size distribution is a range of 0.5 to 100µm particle diameter with a median particle diameter of 50µm. Analysis of particle size distribution by a Malvern Mastersizer 2000 (Malvern Instruments Ltd. Worcestershire, UK) revealed a particle size distribution, as shown in Figure 5.1, with a median diameter of 50µm, but with the largest 10% of particles having diameters greater than 100µm. SEM images of the PEEK powder revealed that it is roughly spherical in nature, as depicted in Figure 5.1. The Malvern Mastersizer 2000 works on the principle of diffraction of a laser beam of a known wavelength, through a solution of the particulate matter to be measured. The PEEK particles were suspended in water for the analysis of particle size distribution. The intensity and scattering pattern of the laser beam was used to calculate the particle size

distribution by the "Mie-theory" which requires knowledge of the refractive index of both the liquid medium and the particles dispersed in it.

5.3 Depositing splats on substrates

5.3.1 Single splat deposition

Single splats sprayed by the HVAF process were deposited with a Browning Aerospray 150 HVAF system. Fuel and gas flows were controlled with an Aerospray controller, whilst a Mark XV Precision Powder Feeder (Powder Feed Dynamics Inc., Berea, OH, USA) with a vibrating screw feed system was used to control powder feed and carrier gas conditions. Vibration was set at 70% of maximum for optimum powder flow. Single splats were collected in a single swipe pass at 0.5 ms⁻¹. A test matrix of 50, 100 and 200 mm nozzle lengths, and spray distances of 50, 100, 150 and 200 mm nozzle at a spray distance of 200 mm. The spray variables used for single splat collection are summarised in Table 5.1

Single splats deposited by the plasma process were sprayed with a Sulzer Metco 7MB plasma system. The powder feeder used was a Praxair 1264 rotating slot powder feeder

HVAF spray conditions		Plasma spray conditions			
Spray distance:	200mm from nozzle to	Spray distance:	80mm from torch to		
	substrate		substrate		
Nozzle type:	100mm barrel	Nozzle type:	8mm G		
Air pressure:	90psi	Nitrogen flow rate:	57 standard litres per		
			minute (SLPM)		
Kerosene flow rate:	Essentially constant,	Hydrogen flow rate:	0 SLPM		
	unmeasured				
Combustion	60-65 psi	Voltage:	55V		
chamber pressure:					
Carrier gas	75 psi	Current:	250A		
pressure:					
Powder feed rate:	7g/min	Carrier gas flow	5.5 SLPM (Nitrogen)		
		rate:			
Powder carrier gas:	Nitrogen	Powder feed rate:	<5g/min		

Table 5.1 Spray conditions for the deposition of HVAF and plasma sprayed PEEK splats.

(Praxair Surface Technologies, IN, USA). The powder was fed at rates below the calibrated level of the controller, and as such is unknown, but were likely in the range of 10 to 20 g/min. Power was supplied by a Plasma Technik PT800 (Sulzer Metco, Winterthur, Switzerland), with current and voltage controlled by a PC100R controller. The gas flows were controlled by an in house system developed at the Centre for Thermal Spray Research, Stony Brook University, New York. The torch was mounted on an industrial robot, with splats deposited in a single pass at a 0.5ms⁻¹. Given the low melting and thermal degradation temperatures of PEEK [97] in comparison to the melting points of common plasma spray powders a low power spray condition was used. A range of between 40 and 65 SLPM of N₂, with and without H₂, and spray distances of 60, 80 and 100mm were investigated to optimise the process, with the conditions above providing the greatest deposition efficiency whilst minimising thermal degradation of the PEEK splats.

5.4 Substrate mounting and temperature control

Substrate temperature has already been shown to have an effect on the morphology of splats [53, 56, 58, 61, 90, 108]. To investigate whether this effect was linked to the glass transition temperature, or the melting temperature of PEEK, splats were collected on polished substrates held at incremental temperatures between 23°C and 363°C. The substrate temperatures are shown in Table 5.2. These temperatures were chosen to give an idea of trends with substrate temperature, and/or for their proximity to certain key properties of PEEK. The ambient temperature when this spraying was performed was 23°C, it was thought that the glass transition temperature of PEEK (143°C) might have an effect on splat properties, so 123°C and 163°C were investigated so that it could be determined with a degree of certainty that the two points were either side of the glass transition temperature (which is more of a range than a fixed point with polymers). The next two temperatures, 230°C and 275°C were chosen to fill the gap in temperatures to the melting point of PEEK (343°C). Again, two temperatures were chosen to bracket the melting point, 323°C and 363°C, ensuring that they could be determined with certainty to be above or below the melting point.

HVAF substrates were mounted within a machined groove on a copper block attached to a laboratory hot plate, a representation of a sample on the copper block is shown in Figure 5.2. The temperature of the copper block was monitored by two K type thermocouples, one clamped directly to the front face of the copper block and the other mounted on an equivalent piece of aluminium to the substrates, bolted in the groove in the same

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Carre.

Temperature	Reason for selection
23°C (ambient)	Ambient conditions are easiest to spray at.
123°C	20°C below the glass transition temperature of PEEK (143°C [109]).
163°C	20°C above the glass transition temperature of PEEK. (143°C [109]).
230°C	A marker to reveal any possible trends.
275°C	A marker to reveal any possible trends.
323°C	20°C below the melting temperature of PEEK (343°C [97]).
363°C	20°C above the melting temperature of PEEK (343°C [97]).

 Table 5.2 Substrate preheat temperatures.



Figure 5.2 Schematic of copper block substrates were mounted on for spraying.

manner as the substrates. After spraying, substrates were removed from the copper block and placed on heat resistant material to cool naturally. No samples were quenched. Once samples had reached room temperature they were placed in a desiccator where they were stored until they were imaged by SEM. Plasma substrates were mounted in an equivalent method to that illustrated in Figure 5.2. This copper block was heated with an element mounted on the back of the block, with block temperature monitored by a K type thermo-couple mounted on the top of the block. Plasma sprayed samples were removed and cooled in the same manner as HVAF samples after spraying.

5.5 Imaging single splats

Standard SEM imaging to provide topographical information was conducted with an Everhart-Thornley detector which uses secondary electrons to generate an image of the surface. These images, however, had an insufficient range of grey scale values, such that images could not be thresholded to isolate single splats from the substrate. Another



Figure 5.3 Two SEM images of the same area, the left image using secondary electrons, the right using back scattered electrons to generate the image.

imaging technique possible with SEM is back scatter imaging, where the energy of elastically back scattered electrons is measured, which is proportional to the atomic number of the material the electron interacts with, giving an image where contrast is provided by atomic weight, with heavy elements showing up lighter, and light elements darker in the image. A secondary electron and back scattered electron image are shown side by side in Figure 5.3. The secondary electron image is depicted in a narrow band of gray scale shades, and splats are comprised of both lighter and darker shades than the substrate. In contrast, in the back scattered electron image, the PEEK splats appeared dark (being essentially light carbon) whist the aluminium substrate was lighter (due to the greater atomic number of aluminium compared to carbon). Despite shading differences, the images provided the same profiles of the single spats, and although some topographical information was lost in the back scattered image, it provided a better image for image analysis.

5.6 Image analysis

To quantify the images of splats collected by SEM, image analysis was undertaken using ImageJ [110] an open source software package designed for use by the scientific community in the quantification and analysis of images generated by optical, electron and x-ray imaging techniques.

Single splat coupons were imaged as-sprayed so as to preserve the single splats present and minimise the risk of introducing artefacts to the images through sample handling. Plasma sprayed samples could be imaged without coating with platinum, but the HVAF samples charged badly and required coating with a thin layer of platinum. It is thought plasma splats did not charge in the same way as HVAF splats due to a layer of conductive carbon which could have formed due to thermal degradation of the surface of the PEEK particles during plasma spraying. This was not further tested.

A random point in the centre of a sample was selected and from that point images were taken after taking semi-random steps, but with care taken not to image the same area twice. Image area was dictated by the area required to get a minimum of about 50 splats, with a minimum view area of 1mm². Back scatter images were used so the splats could be easily differentiated from the aluminium substrate due to the difference in atomic weights.

Figure 5.4 presents the steps that were taken to quantitatively analyse the properties of single splats from the SEM images. The scale bars of the images were measured and referenced to the number of pixels such that lengths and areas could be digitally measured. Once scale was set the images were cropped to remove the information bars. When splats were found to be overlapping they were separated along the boundary of the two splats with a thin white line using the ImageJ software.

The images were then thresholded so that splats (PEEK) were defined in black and the aluminium substrate was defined in white. Images were then "despeckled," a technique where individual pixels surrounded by the opposite colour (i.e. a black pixel surrounded by white pixels or vice versa) were removed.

Images were the analysed and the individual splats were measured for their area, perimeter, Feret diameter, and circularity. Perimeter is a measure of the outside boundary of each splat. Feret diameter is the longest distance between any two points on the boundary of a splat. Circularity is calculated by the formula 4πA/(perimeter²), where A is the area of the splat. A circularity of 1 equates to a perfect circle, and the closer to zero the value the more elongated or fingered a splat is. The area of a splat was computed by adding up the number of pixels in a splat and multiplying by the area of a single pixel as defined by the scale. Splats smaller than 200µm² were not counted as they were determined to be the result of splashing, and not primary splats. This information was exported as a Microsoft Excel[™] spreadsheet. The data in the spreadsheets was summarised and averaged for each image and then for each set of images representing the same variable sets.



Figure 5.4 The process of image analysis (a) is the raw back scatter SEM image, (b) has had the scale digitised, been cropped, and individual splats partitioned where required, (c) reveals the thresholding of the splats, and (d) reveals the final result for analysis after holes are filled and the image is "despeckled."



Figure 5.5 Left, the raised oxide deposits on boehmite. Right, PEEK splats on the same surface as shown on the left.

The data was tested for validity in two ways. Geometric gray-scale shapes with known areas and perimeters were generated with graphics software and then processed with

ImageJ in the same manner as the SEM images of single splats were processed. These tests showed that there was complete agreement between the processed results and the true measurements of the geometric shapes. Single splat images taken with an SEM were then analysed. It was found that with secondary electron images splats could not reliably be differentiated from the substrate by a single gray-scale value, despite the line between splat and substrate being easily distinguishable to the human eye. Back scattered electron images of single splats could easily be distinguished from substrate by a gray-scale thresholding procedure. Back scattered electron images were both manually processed and processed with ImageJ. Variation of the quantified results from the two processing methods was less than 5% in all instances. Variation was the result of shadowing in the SEM images artificially increasing splat areas. This shadowing also led to some smoothing of a portion of the splat perimeter, leading to a slight increase in the quantified circularity.

The boehmitising process, in combination with plasma spraying, left raised oxide deposits, shown in Figure 5.5, on the surface of the aluminium that the thresholding process was not totally capable of separating from splats and splat splashes. It was found that by generating a binary masking image over the area of splats (identifiable by human eye) and adding this mask to the original image the splats could be thresholded in the same manner as splats on a polished or etched surface. The formation of these raised oxide deposits is discussed in section 7.3.

6 Qualitative Splat Analysis

The two spray processes, plasma and HVAF, have very different process parameters resulting in very different splat shapes, as is demonstrated in Figure 6.1. HVAF splats deposited on room temperature substrates, were much less uniform than plasma splats, with uneven spreading and low circularity. In contrast, plasma splats were generally smooth circles or ellipses, with only the smaller particles resulting in fingered, splashed looking splats. Plasma splats also appeared to have surfaces covered with significant pores, possibly a result of degassing of the PEEK particles during spraying, or as a result of degassing of the substrate upon impact. HVAF sprayed splats had a very rough and varied surface in contrast to plasma splats, suggesting that the splats were solid or semisolid upon impact. As HVAF has a cooler flame and higher particle velocities than plasma spraying, HVAF results in lower heat transfer to the particles in flight. HVAF splats also varied in size much more than plasma splats, and had a greater degree of splashing, as evidenced by the large number of small PEEK particles, typically very circular, displayed in Figure 6.1.

Splats deposited on 323°C substrates differed significantly in appearance to those deposited on room temperature substrates, as can be seen in Figure 6.2. HVAF splats still remained larger than plasma splats, and if anything the splashing of HVAF particles on impact increased with increased surface temperature. Of note is that the splats sprayed by HVAF appeared molten, despite the substrate being below the melting point of PEEK (343°C). The HVAF splats were expected to be cooler with higher viscosity than plasma splats, resulting in decreased splashing. The increased splashing is thought to be due to a thin low viscosity layer of PEEK which splashed due to the increased velocity of HVAF sprayed particles relative to plasma sprayed particles.

HVAF splats on 323°C substrates also exhibited smoother perimeters than on room temperature substrates, although still less regular than plasma splats. This was partly due to less adsorbates present on the surface at 323°C and partly due to increased particle melting helping to smooth the edges of the splats. This was in accordance with the results Ivosevic et al. published where both HVOF sprayed polyimide and polyamide splats increased in circularity with increased substrate temperature [56, 60, 111].

Plasma splats deposited on 323°C substrates exhibited similar morphologies to nylon-11 splats deposited on heated substrates [60]. Some splats additionally appeared to have a



Figure 6.1 Left, HVAF single splats deposited on room temperature polished aluminium substrates. Right, plasma single splats deposited on a room temperature polished aluminium substrate.



Figure 6.2 Left, HVAF single splats deposited on a 323° polished aluminium substrates. Right, plasma single splats deposited on a 323°C polished aluminium substrate.

limited "fried egg" aspect, associated with room temperature substrates in the work by lvosevic et al. This suggested that the splats had a molten or semi-molten outer layer with a solid, or at least more viscous, core with the result that the outer layer flowed and spread out on the substrate with the core remaining dense and less spread [65]. There was less splashing or fingering of plasma splats on 323°C substrates. A reduction in fingering of splats and an increased number of disc splats with increased substrate temperature was a trend common across all thermal spray powders [61].

HVAF PEEK splats deposited on a room temperature substrate appeared to have torn apart on impact as opposed to flowing across the surface, suggesting the particles were not melting in flight, and were solid or highly viscous on impact. The highly fingered nature of the splats however conforms well with the morphology of zirconia splats on a room temperature substrate [81] and molybdenum splats deposited on a 200°C substrate [58]. Cedelle and Sampath both saw significantly reduced fingering splats with increased substrate temperature, whilst there was minimal morphology change exhibited between the HVAF splats in Figure 6.1 and Figure 6.2. The significant difference between HVAF PEEK splats on room temperature substrates and any other splat was the non-molten appearance of the splat, whereas all other polymer, metal and ceramic splats appeared to have melted to some extent in flight.

Comparison of plasma splats on room temperature substrates and 323°C substrates revealed significant variations (Figure 6.1 and Figure 6.2). Splats on the room temperature substrate appeared to have a significant degree of porosity within the splat, with large pores on the top surface of the splats. In comparison, no pores were seen on splats deposited on 323°C substrates, suggesting that the increase in substrate temperature drove off adsorbates from the substrate, decreasing splat porosity. The splats deposited on the heated substrate also exhibited a much greater degree of overlapping with each other, possibly a result of post impact melting, or possibly a result of further spreading on impact.

HVAF sprayed splats exhibited a high number of secondary particles on the substrate surface due to splashing of PEEK particles on impact. In comparison, plasma sprayed substrates exhibited very few secondary particles due to splashing, irrespective of substrate temperature. Increased substrate temperature normally leads to reduced splashing of metal and ceramic particles [61], and as such it was expected that there would be reduced splashing of the heated HVAF sprayed substrates. The lack of splashing on plasma splats was probably due to the combination of the lower velocity of the plasma system and the high viscosity of the PEEK particles compared to metals and ceramics [56].

Qualitative examination of splats revealed no significant differences between splats on the polished, etched and boehmitised substrates. This was true for both plasma and HVAF sprayed splats, as is shown in Figure 6.3.



Figure 6.3 PEEK splats on differently pretreated substrates, A, B, and C are HVAF sprayed splats on polished, etched and boehmitised substrates, respectively. D, E, and F are plasma sprayed splats on polished, etched and boehmitised substrates, respectively.

7 Plasma Spray of PEEK Single Splats

7.1 Effect of surface chemistry and morphology on plasma sprayed PEEK splats

Five parameters were considered in the evaluation of the effects of substrate surface chemistry, morphology and temperature on splats. They were the number of splats deposited per square millimetre, the circularity of those splats, and the area, perimeter and Feret diameter of the deposited splats. These parameters were selected as they provided a good overall picture of the splats numerically. The number of splats per square millimetre gives an idea of deposition efficiency on each substrate, and how they compare with each other. The area of each splat defines the degree of spreading that occurs upon impact, and allows examination of whether the experimental variables affect particle spreading on impact. Circularity allows investigation into the degree of fingering that occurs on impact on the different substrates and how far from the ideal disc splat a splat is. Measurement of splat perimeter and Feret diameter allow for internal cross checking, where splat area, perimeter, Feret diameter and circularity all have interrelationships, and could be used to determine processing artefacts and statistical accuracy.

There are three distinct groups of data that can be derived from each variable from the experiments performed. For example, when taking into account the circularity of splats, the effect of surface treatment at constant surface temperature can be examined, as can the effect of thermal treatment on the circularity of splats, and both of these two sets can be further broken down to effects on substrates held at 23°C and at 323°C. Finally the effect of surface temperature with constant treatment can be evaluated. Substrate temperature has been recognised as an important parameter in the formation of single splats and coatings in the thermal spray community, as discussed in section 2.5 [61].

Whilst quantitative analysis of single splat images has allowed much greater information to be extracted from single splat images, the distribution of the raw data is not normal, as illustrated in Figure 7.1. This means that statistical evaluations such as the t-test, confidence intervals and standard deviations cannot be applied to the data. Error bars are included on the graphs that were determined as the standard deviation of the means of sample values, giving an indication of the variability of the data. Consistent trends are

V=vt=List of research project topics and materials



Figure 7.1 Example of the non-normal distribution of splat parameters, HVAF splats on 23°C polished substrates.

repeatably shown across the results, indicating the validity of the data, despite high variability in some data subsets.

Wetting of the PEEK splats on the pretreated substrates may have had an effect on the morphology of the PEEK splats. Contact angle wetting experiments of PEEK on the different substrates were considered, but decided against. This decision was reached because the results of contact angle measurements on a stationary droplet heated slowly through its melting point cannot be compared to the processes occurring when a thermally sprayed particle impacts a substrate at speeds in excess of 200ms⁻¹ for plasma spray, and 500ms⁻¹ for HVAF spray.

7.1.1 Number of splats

For substrates at 23°C, surface treatment type had a significant effect on the number of splats deposited on the surface. It can be seen from Figure 7.2 that the boehmitised surface had fewer splats than the etched surface, which had fewer splats than the polished surface. Comparing the thermally treated samples on 23°C substrates the BT

sample had fewer splats than the ET and PT surfaces, which had similar numbers of splats. Thermal treatment of the different surfaces also affected the number of splats deposited with BT and ET surfaces having more splats than B and E surfaces, respectively, however, PT and P surfaces had similar numbers of splats.

For substrates at 323°C, B surfaces had fewer splats than E and P which had similar numbers, and of the thermally treated surfaces, BT, ET and PT all had similar numbers of splats. Thermal treatment had less of an effect at 323°C, where B had fewer splats than BT, whilst P and E had similar numbers of splats respectively to PT and ET. These results are displayed in Figure 7.3.



Figure 7.2 Number of splats per mm² on a 23°C substrate with different surface pretreatments.



Figure 7.3 Number of splats per mm² on a 323°C substrate with different surface pretreatments.

Trends with (constar	n Treatment ht Temp.)	Trends w (constant	ith Temp. treatment)
23°C	323°C	23°C	323°C
B <e<p< td=""><td>B<e~p< td=""><td>Data</td><td></td></e~p<></td></e<p<>	B <e~p< td=""><td>Data</td><td></td></e~p<>	Data	
BT <et~pt< td=""><td>BT~ET~PT</td><td>Not Comparab</td><td>le</td></et~pt<>	BT~ET~PT	Not Comparab	le
Thermal vs. Non-Thermal treatment (constant Temp.)			
23°C	323°C		
B <bt< td=""><td>B<bt< td=""><td></td><td></td></bt<></td></bt<>	B <bt< td=""><td></td><td></td></bt<>		
E <et< td=""><td>E~ET</td><td></td><td></td></et<>	E~ET		
P~PT	P~PT		

Table 7.1 Summary of plasma "number of splats" results.

Unfortunately it was not possible to reliably compare the number of splats deposited at 23°C and those deposited at 323°C because they were deposited on different spray runs. The nature of the PEEK powder was that powder flow rate was somewhat variable, being affected by uncontrollable variables such as humidity and static charge build up, thus whilst the number of splats sprayed in the same pass could be compared to each other, those sprayed during two independent passes could not.

As shown above, surface pretreatment had a significant effect on the properties of splats deposited on an aluminium surface. Each surface pretreatment resulted in a different surface chemistry, morphology and thickness of the oxide layer present on the surface, as was discussed in section 4.

The number of splats per unit area deposited on room temperature substrates was highly dependent on the pretreatment of each substrate and the resulting surface chemistry. The resultant surface chemistry was discussed fully in section 4.1. A boehmitised surface had the fewest splats deposited (40% of those on a polished substrate), followed by the etched surface (70% of those on a polished substrate), with the polished surface collecting the most. The low number of splats adhered to the B surface was due to the properties of the boehmitic oxide layer present on the aluminium surface. Boehmite is a meta-stable hydrated oxide which dehydrates when sufficient thermal energy is supplied [22]. Particle impacts could result in dehydration of boehmite, releasing water vapour, which would reduce the number of splats that bond with the surface. Additionally, the low particle numbers adhering to boehmitic surfaces was in agreement with the work of Trompetter, who reported that HVAF sprayed NiCr particles did not adhere to boehmitic aluminium substrates, but did adhere to electrochemically formed aluminium oxide layers [103]. The etched surface had a greater number of splats collected, despite the presence

of aluminium hydroxide and chemisorbed water on the surface. The hydroxide can be converted to oxide by thermal energy, releasing water, and the chemisorbed water can be vaporised by the thermal energy generated and transferred from splat impacts, resulting in fewer splats adhering. The polished surface had the lowest degree of chemisorbed water of the three treatments, as discussed in section 4.1.5, resulting in the largest number of splats adhering to this surface. Thus, the pretreatment that resulted in the lowest amount of chemisorbed water and hydroxide on the surface (as determined by XPS) had the highest number of splats, whilst increasing the amount of hydroxide and chemisorbed water on the surface correlated to a decreasing number of splats adhered to the surface.

Thermal treatment of the samples, resulting in the BT, ET and PT surfaces, drove off the physisorbed water and some of the chemisorbed water, although subsequent time at ambient conditions resulted in some re-adsorption of water to the substrates. The thermal treatment of B surfaces was not hot enough for the full conversion of boehmite to γ -Al₂O₃ to occur, as evidenced by the fact that the samples with BT pretreatment frequently exhibited different splat morphologies to the samples with ET or PT treatments. Some conversion however did take place as splats on a B surface often differed from those on a BT surface. Thermal treatment of E and P surfaces resulted in ET and PT samples having very similar surface chemistries, and despite the hugely different surface morphologies of the two treatments they collected similar numbers of splats, showing that at 23°C surface chemistry dictated the number of splats deposited. Thermal treatment of E surfaces greatly reduced the hydroxide peak and removed any chemisorbed water (as shown in section 4.1.5). This meant that there was less aluminium hydroxide present on the surface available to generate water vapour, thus the thermal energy transferred and released on impact released less water vapour, increasing the number of splats deposited compared to an etched surface.

When spraying onto substrates heated to 323°C different trends were seen, B had fewer splats (75% of those on a polished substrate) than E and P, which had similar numbers (~80 per mm²). This was essentially due to the further thermal treatment of heating the substrates up to 323°C. This drove off adsorbates from the surface of the E and P samples, the B surface, however, required much more time to achieve full conversion to an oxide surface, thus reducing the number of splats that adhered to it. Spraying onto the thermally treated surfaces at 323°C revealed that the combination of the two thermal treatments effectively completed the conversion, with no significant difference between the number of splats collected on each of the three thermally treated surfaces. This trend

was mirrored in the comparison of B to BT, E to ET and P to PT, where thermal treatment of B to BT increased the number of splats deposited, but E and ET, P and PT had similar numbers of splats to each other. The varying magnesium contents of the 6 substrates had no effect on the number of splats adhering to the substrates.

7.1.2 Splat circularity

When substrates were held at 23°C splats deposited on a boehmitised surface were shown to have circularity about 60% that of etched and polished surfaces (circularity ~0.52), which had similar circularities, as shown in Figure 7.4. Thermal treatment showed a similar trend, with BT splats having circularity about 70% that of ET and PT splats, which had similar circularity (circularity ~0.52). Thermal treatment affected the B surface, with BT splats exhibiting greater circularity than B splats, whilst E and ET, and PT and PT splats showed no difference in circularity.

Substrates held at 323°C showed greater variability, as such B, E and P surfaces all exhibit similar splat circularities (circularity ~0.55). The thermally treated surfaces show reduced variability, and it is reasonable to say that splats on the BT surface had a circularity about 75% than those on ET and PT surfaces, which had similar circularity. Thermal treatment of the B, E and P surfaces resulted in no change in the circularity of splats deposited on 323°C aluminium surfaces. For almost all pretreated surfaces, the increase in temperature from 23°C to 323°C resulted in an increase in circularity, the exception was the etched surfaces, where no significant difference in circularity was observed between 23°C and 323°C.

The circularity distribution diagrams, presented in Appendix A, showed that the circularity distribution is basically triangular for all the substrate pretreatments and substrate temperatures with large numbers of splats with high circularity and decreasing numbers of splats with lower circularity. The main points of interest were the spread of the circularities, also presented in Figure 7.4, where typically the 323°C substrates had a greater spread in circularity data than substrates at 23°C. This increased spread was possibly the result of increased splat melting resulting in a greater circularity for some splats.

On room temperature substrates, splat circularity was lower on B surfaces than on E and P surfaces which had similar circularities. The low circularity on B surfaces was likely to have been due to degassing of the substrate due to particle and plasma energy. Despite the significant morphological difference between E and P surfaces, they had similar

circularities, indicating that surface chemistry and adsorbates governed splat flow on impact and thus circularity. The same trend was observed with the thermally treated surfaces (BT, ET and PT) with BT producing less circular splats, again a factor of surface wettability and the incomplete conversion of the BT surface from boehmite to oxide layer and the associated release of water vapour due to the thermal energy related to splat impact. Again, the magnesium content of the oxide layer has no effect on splat circularity.

Thermal treatment of the B surface, forming a BT surface, resulted in more circular splats. There was no difference in circularity between E and ET or P and PT surfaces, again despite the different roughnesses ($Ra_E 253nm$, $Ra_{ET} 254nm$, $Ra_P 12nm$, $Ra_{PT} 12nm$ respectively). At 323°C there is no difference in circularity between any of the treatments, and thermal treatment also has no effect. Increasing the surface temperature from 23°C



Figure 7.4 The effect of surface pretreatment on splat circularity.

Trends with Treatment (constant Temp.)		Trends with Temp. (constant treatment)			Surface Roughness
23°C	323°C	23°C		323°C	Ra (nm)
B <e~p< td=""><td colspan="2">B<e~p b~e~p<="" td=""><td>۷</td><td>В</td><td>34</td></e~p></td></e~p<>	B <e~p b~e~p<="" td=""><td>۷</td><td>В</td><td>34</td></e~p>		۷	В	34
BT <et~pt bt~et~pt<="" td=""><td>E</td><td>۲</td><td>E</td><td>253</td></et~pt>		E	۲	E	253
Thermal vs. Non-Thermal treatment		Р	<	Р	12
(constan	nt Temp.)	BT	<	BT	18
23°C	323°C	ET	<	ET	254
B <bt b~bt<="" td=""><td>PT</td><td><</td><td>PT</td><td>12</td></bt>		PT	<	PT	12
E~ET E~ET					
P~PT					

Table 7.2	Summary	v of	plasma	"splat	circularity	" results.
	• • • • • • • •		piaoina	opiai	onoanarry	

to 323°C however has a significant effect, with all surfaces except E having more circular splats at 323°C. More circular splats at 323°C were probably primarily the result of melting of the splats due to the kinetic energy transfer to thermal energy upon impact, and possibly improved by reduced adsorbates on the surface. These effects will be discussed more fully in section 7.2.

7.1.3 Mean area of a splat

At 23°C splat area was shown to be affected by surface pretreatment. To minimise the effect of position variation in the plasma plume on the particles being deposited, and hence the splat area, the five sample sites were all selected from an area central to the deposition area. Three typical splat area distribution curves are shown in Figure 7.5, with all splat area distribution diagrams presented in Appendix B. Comparative quantitative analysis of splat area required the focus to be placed upon mean splat area but the distribution diagrams to provide some qualitative information. B surfaces especially, but all to an extent, showed a bimodal distribution with a significant spike of splats around 500µm², with the main peak centred between 3000 and 4000µm², with significantly fewer splats over 4000µm² on a B substrate. Other than the spread of the data, the main trend evident in the distribution diagrams was the form, which was essentially a normal distribution curve with a low peak on the smaller area side. This was likely the result of smaller than mean, essentially molten, particles adhering to the substrates, whilst larger than mean particles will not be as molten and less likely to adhere. Boehmitised surfaces had splats 80% the area of etched and polished surfaces, whose splats have similar area $(\sim 2900 \mu m^2)$. However thermally treated surfaces show no difference in area as BT, ET and PT surfaces all had splats of similar area (~2800µm²). Thermal treatment of the surfaces did not result in a significant change in splat area for any of the pretreatments.

Samples that were held at 323°C during spraying also showed a difference between pretreatments. B surfaces had splats 55% the area of polished splats, whilst E surfaces had splats 75% the area than those on P surfaces. For thermally treated surfaces, there were no significant differences between BT and PT surfaces. The ET surface had splats 75% the size of splats on PT and BT surfaces (~3500µm²), but due to the variation of BT and PT splat area, ET cannot be claimed to be significantly smaller.

In all, there was no significant difference in splat area between these three surfaces. Splat area appeared to increase for P and PT surfaces with increasing substrate temperature, but did not appear to change with increasing temperature for any of the other treatments investigated.





Figure 7.5 Typical distribution diagram for splat areas on 23°C substrates.

Figure 7.6 The change in splat area with changing substrate pretreatment.

Trends with (constar	Trends (consta	s wi ant t	th Temp. reatment)			
23°C	23°C 323°C			323°C		
B <e~p< td=""><td>B<e<p< td=""><td>В</td><td>2</td><td>В</td></e<p<></td></e~p<>	B <e<p< td=""><td>В</td><td>2</td><td>В</td></e<p<>	В	2	В		
BT~ET~PT BT~ET~PT		E	2	E		
Thermal vs. Non-Thermal treatment		Р	<	Р		
(constar	nt Temp.)	BT	~	BT		
23°C	323°C	ET	~	ET		
B~BT	B <bt< td=""><td>PT</td><td><</td><td>PT</td></bt<>	PT	<	PT		
E~ET	E~ET					
P~PT	P~PT					

Table 7.3 Summary of plasma "splat area" results.

Splat area was also affected by surface treatment. Splats sprayed onto a B surface at room temperature surface had lower area than splats deposited on E or P surfaces at

room temperature, which had similar areas. This suggested that degassing of the boehmite surface restricted the flow of the splat after impact. Again surface morphology had no effect, as splats on E and P surfaces with different morphologies had similar areas. The thermally treated surfaces had no effect on splat area with splats on BT, ET and PT surfaces all having similar areas. These two results suggested that splat area was affected by surface chemistry and not morphology, but particle properties may have a greater significance here than for number of splats adhering, where surface chemistry of the surface was more strongly governing. Surfaces at 323°C produced a similar trend, with splats on B, smaller than on E, which were smaller than on P surfaces. The low area on B surfaces was again due to the chemistry of the surface and associated degassing. The difference between E and P on 323°C substrates, when there was no difference on 23°C substrates, suggested that surface morphology restricted splat flow on E substrates at elevated temperatures, where it did not at room temperature. In a similar manner, substrates at 323°C again revealed ET splats had lower area than BT and PT splats, suggesting that the high surface roughness of ET surfaces restricted splat flow. This again showed that surface chemistry governs splat area on room temperature substrates, but surface roughness also affected splat spreading on heated substrates. Thermal treatment affects splat area on B surfaces at 323°C, where BT surfaces resulted in larger splats than on B surfaces, and it is possible that the same was true on room temperature substrates, but the large variability of splat area on B and BT surfaces resulted in this not being statistically significant. There was no difference between E and ET or P and PT surfaces at either 23°C or 323°C.

The increase in splat area associated with the increase of substrate temperature on the P and PT substrates was likely caused by splat melting, with low surface roughness allowing unrestricted spreading. The effect of substrate temperature on splat morphology will be discussed more fully in section 7.2.

7.1.4 Splat perimeter

At 23°C, substrate treatment can be seen to have had an effect on the perimeter of splats. Boehmitised splats had perimeters 15% greater than etched and polished splats, which had similar perimeters (~260 μ m). Similarly for the thermally treated surfaces, BT splats had perimeters 25% greater than ET and PT splats, which have similar perimeters of (~250 μ m). There is no significant difference in splat perimeter between thermally treated and non-thermally treated surfaces at 23°C.



Figure 7.7 The effect of surface pretreatment on splat perimeter.

Trends with (constan	Trend (consta	s wi ant t	th Temp. reatment)	
23°C	323°C	23°C		323°C
B>E~P	B~E~P	В	^	В
BT>ET~PT BT~ET~PT		E	~	E
Thermal vs. Non-7	Р	~	Р	
(constan	t Temp.)	BT	~	BT
23°C	323°C	ET	~	ET
B~BT	B~BT B <bt< td=""><td>~</td><td>PT</td></bt<>		~	PT
E~ET E~ET				
P~PT P~PT				

 Table 7.4 Summary of plasma "splat perimeter" results.

At 323°C there were fewer differences between the different surfaces. Splats on B substrates had perimeters 80% of those on a P substrate, whilst those on an E substrate had perimeters 90% that of splats on P substrates. However, perimeter variability made these differences statistically insignificant. Similarly the differences in perimeter on BT, ET and PT substrates were statistically insignificant. Thermal treatment of the surface resulted in larger perimeter splats (by 30%) on BT compared to B, but E and P were no different to ET and PT respectively. Splats deposited on a boehmitised surface at 23°C had perimeters 45% greater than splats deposited on a B surface at 323°C, but there was no significant difference with temperature for any of the other five pretreatments.

Splat perimeter showed some change with surface pretreatment. Despite the smaller area of splats on a B surface at 23°C, the perimeters of these splats were 15% larger than the perimeters of splats on P or E surfaces, which were of similar size (~260µm). This increase in perimeter was linked to the low circularity of these splats. Splats

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deposited on a BT surface at 23°C also had larger perimeters than those on ET and PT surfaces, which were of similar perimeters. There was no difference in splat perimeter between B and BT, E and ET and P and PT samples held at 23°C. Substrates held at 323°C resulted in no difference in perimeter for B, E and P, and BT, ET and PT samples. However, splats on a B surface had smaller perimeters than those on a BT surface when the substrates were held at 323°C. This appears inconsistent with the fact that B, E and P splats had similar perimeters, and BT, ET and PT splats had similar perimeters, and P and PT and E and ET surfaces resulted in splats of similar perimeter. However, as generalisations were required, and statistical variation had to be taken into account, whilst many surfaces had splats with "similar" perimeters, splats deposited on B and BT surfaces at 323°C did differ in perimeter. This difference was the result of the larger area of BT splats compared to B splats at 323°C, a trend that was consistent with splat diameter as shown in section 7.1.3. Increasing the substrate temperature resulted in a decrease in splat perimeter on B surfaces, but not on any of the other five surfaces. This decrease in perimeter with substrate temperature for the B surface was likely to be due to the substrate preheat driving off adsorbates, resulting in more even splat spreading and less fingering. Again magnesium content of the surface had no effect on splat morphology.

7.1.5 Splat Feret diameter

Surface treatment of the aluminium samples had no effect on the Feret diameter of splats when the substrates were held at 23°C. The boehmitised, etched and polished surfaces all had similar diameter splats (~79 μ m), as did the BT, ET and PT splats (~79 μ m). Thermal treatment of a given surface also had no effect, with B and BT, E and ET and P and PT surfaces all having splats with similar Feret diameters (~79 μ m).

The above trend is not continued at 323° C. At 323° C B splats had Feret diameters 75% that of P splats, whilst E splats had Feret diameters 90% that of P splats (~81µm). Thermally treated samples however didn't differ with BT, ET and PT splats all having similar Feret diameters (~82µm). Thermal treatment from B to BT resulted in 35% larger diameter splats, but there was no difference between E and ET, and P and PT splats respectively.

Substrate temperature only affected samples with a B surface, where splats deposited at 323° C had Feret diameters 80% of those deposited on a 23° C substrate (74µm). The other five surface treatments showed no difference in diameter between the two temperatures. Consistent with splat area and perimeter, the Feret diameters of splats on



Figure 7.8 The effect of surface pretreatment on splat Feret diameter.

Trends with (constan	Trend (const	ls wi ant t	th Temp. reatment)	
23°C	323°C	23°C		323°C
B~E~P	B <e<p< td=""><td>В</td><td>></td><td>В</td></e<p<>	В	>	В
BT~ET~PT	E	~	E	
Thermal vs. Non-7	Р	~	Р	
(constan	t Temp.)	BT	~	BT
23°C	323°C	ET	~	ET
B~BT	B~BT B <bt< td=""><td>~</td><td>PT</td></bt<>		~	PT
E~ET E~ET				
P~PT				

Table 7.5 Summary of plasma "splat Feret diameter" results.

B surfaces were smaller than on BT surfaces, but there were no differences between E and ET or P and PT surfaces. This indicated that thermal treatment had a greater effect on B surfaces than on P or E surfaces. The increase in temperature from 23°C to 323°C resulted in a decrease in splat Feret diameter on B surfaces, and no change for the other five surfaces, as mentioned already, this was due to the increased circularity associated with the increase in substrate temperature.

7.2 Effect of substrate temperature on plasma splat properties

The effect of surface temperature on splat area is represented in Figure 7.9. There was a general linear trend showing increasing splat area with increasing substrate temperature. This was an expected result, but a much steeper trend was expected. The increasing area is thought to be due to greater spreading of the splats on impact due surface adsorbates being driven off by the higher substrate temperatures and a lower temperature difference between the splat and the substrate reducing the driving force of

the cooling of the splat such that cooling and solidification would not affect the spreading of the splat. It was also expected that an increase in circularity and diameter would correspond to the increasing area, however, Figure 7.10, and Figure 7.11 showed that these trends were not recorded. This result indicated that for plasma spraying of PEEK splat diameter and circularity are governed more strongly by the process parameters of the plasma system and the substrate surface chemistry and not influenced by the substrate temperature. Despite the measured variables showing little difference with increasing substrate temperature, this does not mean that unmeasured variables such as splat crystallinity, porosity at the splat/substrate interface, and adhesion of singles splats was not affected by the substrate temperature.

In Figure 7.12 splats are shown to begin exhibiting the "fried egg" phenomenon, as modelled and predicted by Ivosevic et al. [56] on substrates heated to 275°C and above, this is due to particles having a high viscosity core that does not spread upon impact, whilst the lower viscosity outer layer spreads like the white of a fried egg around the yolk.

Qualitatively, splats appeared to have a smoother perimeter (more circular) with increasing substrate surface temperature, in lieu of actual splashing at lower temperatures, suggesting that increased surface temperature did reduce splashing, consistent with Fukumoto, Sampath, and Ivosevic [56, 58, 79]. This trend was less obvious in this study due the higher viscosities associated with PEEK and polymers in general compared to metal and ceramic single splats examined in the other studies.

Splats also appeared to have fewer macro pores at substrate temperatures of 230°C and above as shown in Figure 7.12. This was likely due to the lower adsorbate concentrations on elevated temperature substrates resulting in reduced degassing, which in turn resulted in fewer pores in the PEEK splats.

Finally, as substrate temperature increased, the degree of particle overlap also increased, although this was negated in the results due to the image processing technique employed. The degree of overlap may have significance in regard to the degree of particle melting, whether it occurred in flight, on impact, or post impact. A quantifiable parameter for degree of overlap may provide results in this area, but was not investigated for lack of a quantifiable parameter.



Figure 7.9 Mean areas of single splats with increasing substrate temperatures.



Figure 7.10 Circularity of plasma sprayed splats with increasing surface temperature.



Figure 7.11 Feret diameter of plasma sprayed splats with increasing surface temperature.



Figure 7.12 Splats deposited on a polished substrate by plasma spray at increasing substrate temperatures.

7.3 Plasma splats discussion and summary

Single splats were evaluated as to how they were affected by three sets of parameters – surface roughness, surface chemistry and temperature of the substrates they were deposited on. When splats were deposited by the plasma spray process it was found that the number of splats deposited was primarily affected by the surface chemistry of the substrate. This can best be summarised as the lower the amount of hydroxide and chemisorbed water on the surface of the substrate the more splats adhered. Splat circularity was found to be affected by surface chemistry on room temperature substrates,

whilst surface chemistry had no effect on substrates held at 323°C. Again the role of hydroxide and chemisorbed water on the surface was apparent, but splat circularity exhibited a lower sensitivity to these than the number of splats deposited. Circularity of splats was also affected by substrate temperature, with splats on 323°C substrates having greater circularity than those deposited on room temperature substrates. Splat area showed some sensitivity to the effect of surface chemistry, with less hydroxide and chemisorbed water in the oxide layer resulting in larger area splats. Splat perimeter and Feret diameter showed lower sensitivity than splat area to surface chemistry, but both showed decreased values for boehmitic surfaces, which had the greatest level of hydroxide and adsorbed water on the surface. It is important to understand that the chemisorbed water was chemically bonded to the aluminium oxide/hydroxide surface, and remained bonded to the surface at high vacuum on the order of 1×10^{-7} Torr. Chemisorbed water is a chemical constituent on the surface, and unlike a solvent that is easily evaporated, it requires temperatures in the range of 100°C to 200°C for desorption to occur. Nor was chemisorbed water the only influence, as shown by the fact that BT surface substrates resulted in splats of improved properties over B surface substrates, despite a higher level of chemisorbed water on the BT surface.

Interestingly, splat area, perimeter and Feret diameter were not affected by substrate temperature. On polished surfaces, splat Feret diameter and circularity showed no obvious trend with increasing substrate temperature. Splat area, however, showed a slight increase with increasing substrate surface temperature, but within the variability of the results. The presence of magnesium on some surfaces, notably ET, P and PT, had no affect on splat properties.

Further proof that dehydration of the oxide layer occurred with thermal energy was exhibited by the B and BT substrates. The B and BT substrates had a boehmitic layer 226nm thick as determined by ion beam analysis. XPS analysis of the B and BT surfaces could only tell us about the top 5 to 10nm of this surface. The adhesion and bonding occurred at this top surface layer that XPS could detect, but there was a thick layer of AlOOH which can be dehydrated to form water. Dehydration of boehmite occurs according to equation 7-1.

Equation 7-1 2AlOOH \rightarrow γ -Al₂O₃ + H₂O



Figure 7.13 Boehmite blisters observed after the thermal spraying process.

Wefers reported the activation energy for the dehydration reaction as between 220 and 325kJ/mol, with variation caused by the temperature of formation of the boehmite [22]. Boehmite requires temperatures of over 400°C and sufficient time for equilibrium conditions to be established for conversion to γ -alumina to take place [22]. Ion beam analysis and XPS showed no difference between B and BT substrates, whilst qualitatively they produced different splats, where the BT substrates had been thermally soaked for over 60 minutes at 350°C, as discussed in section 3.2.4.

Boehmitised, and boehmitised and thermally treated substrates were found to have blisters on the surface, as shown in Figure 7.13, after thermal spraying. These blisters were present on both B and BT substrates, held at 23°C and 323°C, and on substrates sprayed by both the plasma and HVAF techniques. The blisters were more pronounced on substrates sprayed by plasma. These blisters were examined by EDS analysis and found to have the same composition as the oxide layer, with no PEEK present. Two types of blisters were predominant, domes and "volcanoes". Both types of blisters are thought to form as a result of dehydration of the boehmitic surface, caused by the heat transferred to the substrates by the thermal spray torches. It is postulated that as the AIOOH forms Al₂O₃ and H₂O the water is released as water vapour, and when this reaction occurred below the surface, there will be cases where the water vapour is unable to diffuse out leading to blisters forming on the surface. Domes are then the result of vapour pockets below the surface deforming the surface oxide, yet having insufficient pressure to rupture the oxide layer over the top, whereas "volcanoes" were the result of the pressure in a vapour pocket exceeding the strength of the covering oxide layer and breaching the oxide layer, resulting in domes with a collapsed crater in the centre. This theory of blister formation is consistent with the result that more domes and "volcanoes" were found on plasma sprayed substrates than were found on HVAF sprayed substrates.

The domes and "volcanoes" cannot be due to contamination of the PEEK powder as they were only observed on B and BT substrates that were sprayed alongside etched and polished substrates that exhibited no blisters. Whilst the mechanism of formation of the blisters is only conjecture in association with the observed phenomenon, blister formation indicates significant changes occurring to the B and BT substrates during spraying. It is likely that blister formation was a result of dehydration of the boehmite layer, resulting in the release of water vapour. This release of water vapour will greatly affect the adhesion, spreading and splat morphology of PEEK splats.

8 HVAF Spray of PEEK Single Splats

8.1 Effect of surface chemistry and morphology on HVAF sprayed PEEK splats

8.1.1 Number of splats

For substrates held at 23°C, different surface pretreatments had no effect on the number of splats deposited on the surface by HVAF spraying. Thermal treatment of the surfaces also had no effect on the number of splats deposited, with all substrates having about 65 splats per mm². These results are displayed in Figure 8.1. Substrates held at 323°C were, however, affected by variations in surface pretreatment. As shown in Figure 8.2 E surfaces had 60% of the splats on a P surface, whilst B surfaces had 75% the number of splats deposited on a P surface (116 per mm²). This trend was repeated with the thermally treated surfaces with ET having 65% of the number of splats on a PT surface, and BT having 80% of the number of splats on a PT surface (110 per mm²). However, there was no difference between the thermally treated and non-thermally treated samples, with B and BT, E and ET and P and PT surfaces having similar numbers of splats. Due to the 323°C runs being performed separately to the 23°C passes, it was not possible to compare the number of particles deposited at the two temperatures due to the variability of powder feed rate due to humidity and powder static charge among other uncontrollable environmental factors.

For substrates heated to 323°C, the greatest number of splats were deposited on the smoothest surfaces (P and PT), and the fewest on the roughest surfaces (E and ET). There was no significant difference between the number of splats deposited on the thermally treated pairs (B and BT etc.), but significant differences between the pairs. The surface chemistries of the 6 surfaces all differ, as is discussed in section 4.1.5, but the trend differs from that seen for plasma sprayed splats on 23°C substrates (section 7.1.1), and in this case decreasing surface roughness resulted in increased splats deposited. For plasma sprayed splats, it appeared that decreasing the aluminium hydroxide and chemisorbed water on substrates resulted in an increased numbers of splats. Additionally, E and ET were shown to have very different surface chemistries, yet for HVAF at 323°C they collected similar numbers of splats, whilst plasma spray at 23°C was more strongly surface morphology (roughness) dependent, whilst plasma at 23°C was more


Figure 8.1 Effect of surface pretreatment on the number of splats deposited by HVAF on room temperature substrates.



Figure 8.2 Effect of surface pretreatment on the number of splats deposited by HVAF on substrates held at 323°C.

Trends with Treatment (constant Temp.)		Trends w (constant	ith Temp. treatment)
23°C	323°C	23°C	323°C
B~E~P	E <b<p< td=""><td></td><th></th></b<p<>		
BT~ET~PT	ET <bt<pt< td=""><td>Data</td><th></th></bt<pt<>	Data	
Thermal vs. Non-Thermal treatment (constant Temp.)		Not Compa	rable
23°C	323°C		
B~BT	B~BT]	
E~ET	E~ET		
P~PT	P~PT]	

Table 8.1	Summar	v of HVAF	"number	of s	plats"	results.
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Pretreat	Ra
ment	(nm)
В	34
BT	18
E	253
ET	254
Р	12
PT	12



strongly surface chemistry dependent. Further, this suggested that at higher particle temperatures substrate morphology governed the number of splats adhering, whilst cooler particle temperatures resulted in substrate surface chemistry governing the number of splats adhering.

8.1.2 Splat circularity

Substrates held at 23°C showed some variation with different pretreatments, B splats had 70% the circularity of P splats, whilst E splats had 90% the circularity of P splats (0.33). The thermally treated substrates, however, exhibited a different trend, where BT, ET and PT surfaces all had splats of similar circularity (~0.24). Thermal treatment resulted in less circular splats for both the E and ET, and P and PT pairs, whilst thermal treatment did not affect circularity for the B and BT pair.

HVAF splats were all significantly less circular than plasma spray deposited splats, irrespective of substrate pretreatment or substrate temperature. This was a result of the significantly higher impact velocities of the HVAF particles (500ms⁻¹ to 600ms⁻¹) compared to plasma particles (200ms⁻¹ to 400ms⁻¹) and the effective fracture of the HVAF sprayed particles upon impact.

Circularity distribution diagrams are presented in Appendix A. These show that circularity distribution has essentially a triangular distribution, with large numbers of splats of low circularity and decreasing numbers of splats with higher degrees of circularity. This was the opposite shaped triangle to that of the plasma spray splat circularity distribution diagrams.

At 323°C the splats behaved differently with the pretreated substrates. Splats on an E surface were 85% the circularity of splats on P and B substrates which had similar circularities (~0.45). This trend was repeated on the thermally treated surfaces, with ET producing splats 85% the circularity of splats on BT and PT substrates, which had circularities of about 0.46. Unlike the room temperature substrates, thermal treatment had no effect on the circularity of splats, so B and BT, E and ET and P and PT splats did not differ in circularity. All substrates had more circular splats when they were held at 323°C, but with E and P surfaces having the lowest sensitivity to substrate temperature change.

At 23°C, substrate pretreatment had a significant effect on splat circularity. It was found that splat circularity increased from B, to E, to P surfaces. This was due to the B surface



Figure 8.3 Effect of surface pretreatment on the circularity of HVAF sprayed PEEK splats.

Trends with Treatment (constant Temp.)		Trends with Temp. (constant treatment)		
23°C	323°C	23°C		323°C
B <e<p< td=""><td>E<p~b< td=""><td>В</td><td><</td><td>В</td></p~b<></td></e<p<>	E <p~b< td=""><td>В</td><td><</td><td>В</td></p~b<>	В	<	В
BT~ET~PT	ET <pt~bt< td=""><td>E</td><td><</td><td>E</td></pt~bt<>	E	<	E
Thermal vs. Non-Thermal treatment		Р	<	Р
(constan	it Temp.)	BT	<	BT
23°C	323°C	ET	<	ET
B~BT	B~BT	PT	<	PT
E>ET	E~ET			
P>PT	P~PT			

Table 8.2 Summar	y of HVAF "	circularity"	results.
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having the highest level of hydroxide and chemisorbed water on the surface, with E surfaces having less, and P surfaces the least, thus splats impacting a P surface were able to spread uninhibited, resulting in more circular splats. There was no significant difference between the thermally treated surfaces at 23°C. Although there was no significant difference between the B and BT thermal treatment pair, in the case of E and T and P and PT, thermal treatment resulted in a significant decrease in circularity. This decrease in circularity is inexplicable, and likely due to statistically insignificant increases in splat area and Feret diameter (as discussed in following sections) that have combined to form a statistical anomaly of significance in this case.

At 323°C surface roughness appeared to govern splat circularity, with E and ET surfaces having splats with the lowest circularity, and B, BT, P and PT surfaces having splats of similar circularity and similar surface roughness. At 323°C, thermal treatment did not affect splat circularity. As is consistent with all the HVAF results substrate temperature had the most significant effect, with splats on 323°C substrates being much more circular than substrates with the same pretreatment at 23°C. This was a result of the splats

melting on impact with the 323°C substrates and the subsequent slow cooling allowing relaxation and recovery of splats along with recrystallisation, forming a more energetically stable shape, rather than being quenched in a non-equilibrium condition, as happened to splats sprayed onto a room temperature substrate. This is discussed in more detail in section 8.1.3 and 8.2.

8.1.3 Average area of a splat

Room temperature substrates showed no difference in splat area between the different pretreatments used, with B, E and P, and BT, ET and PT all having similar area splats to each other (~3500µm²). As shown in Figure 8.4 there was also no difference with thermal treatment of the surfaces, with B and BT, E and ET and P and PT all having splats of similar area. At 323°C the same trend was observed, with no significant difference in splat area between the six pretreated surfaces, and thermal treatment had no effect.

Splat area distribution diagrams are presented in Appendix B. These showed that the main difference between the room temperature substrates and the 323°C substrates was the number of large splats, with room temperature substrates having a far greater number of large splats on the surface. The distribution diagrams all take on a similar form, with a peak at a low splat area with a low shoulder proportional to the number of larger splats on each substrate. The large deviation from normal required comparison of the mean splat area to the median splat area. Comparison of Figure 8.4 through Figure 8.7 showed that although the mean and median values differed significantly, the same trends were exhibited, whereas splats on room temperature substrates were on average 300% larger than on heated substrates. The significantly higher medians of B and ET surfaces were the result of a greater spread and more uniform distribution than on the other substrates, as can be seen from the distribution diagrams in Appendix B, although no mechanism for this observation has been identified.

The one result of note was the large decrease in splat area with increasing substrate temperature, with splats deposited at 323°C being much smaller than splats deposited on room temperature substrates irrespective of surface pretreatment. Surface pretreatment had no effect on the area of splats sprayed by HVAF onto substrates held at 23°C or 323°C, although there was a high degree of variation in the area of the splats on all of the pretreated surfaces at 23°C. There is a hint at surface roughness/morphology affecting splat area on substrates held at 323°C, in a similar way to the number of splats deposited, but given the variability of the area it cannot be considered as significant. The

variability of splat area was primarily determined by the size of PEEK particles that impacted and adhered to the aluminium surfaces. The large decrease in area with increasing surface temperature is remarkable and counter-intuitive. It was expected that increased substrate temperature would result in larger, and more circular splats, due to post impact melting and spreading, and reduced adsorbates on the surface reducing the resistance to spreading. The results showed that splats deposited at higher temperatures were rounder, but also smaller than those deposited on room temperature substrates. The large decrease in splat area when the substrate temperature was raised to 323°C is thought to be due to two phenomena. Firstly splats sprayed onto a substrate above the glass transition temperature (T_g, 143°C for PEEK) will then cool slowly through the T_g allowing the PEEK to crystallise. Crystallisation of the splats results in a lower specific volume, causing the splats to shrink. Splats sprayed onto a substrate below the T_g of PEEK will quench through the transition, resulting in amorphous splats with only thermal contraction reducing their size. A higher substrate temperature will also affect the viscoelastic properties of the PEEK splats, and could allow relaxation and recovery of residual stresses from the highly spread state just after impact, whereas quenching of splats on a 23°C substrate might result in solidification in the spread state and residual stresses within the splat.



Figure 8.4 Effect of surface pretreatment on mean area of HVAF sprayed PEEK splats.



Figure 8.5 Effect of surface pretreatment on mean area of HVAF sprayed PEEK splats on aluminium held at 323°C.

Trends with Treatment (constant Temp.)		Trends with Temp. (constant treatment)		
23°C	323°C	23°C		323°C
B~E~P	B~E~P	В	>	В
BT~ET~PT	BT~ET~PT	E	>	E
Thermal vs. Non-7	Р	>	Р	
(constan	t Temp.)	BT	>	BT
23°C	323°C	ET	>	ET
B~BT	B~BT	PT	>	PT
E~ET	E~ET			
P~PT	P~PT			

Table 8.3 Summary of HVAF "splat area" results.







Figure 8.7 Effect of surface pretreatment on median area of HVAF sprayed PEEK splats on aluminium held at 323°C.

8.1.4 Splat perimeter

Substrates held at 23°C showed some sensitivity to surface pretreatment. Splats on a B surface had the largest perimeter (454µm), whilst splats on E and P surfaces had similar perimeters (~370µm), that might be lower, but the broad scatter of the splat perimeter data made it inconclusive. The thermally treated surfaces also returned different splat perimeters, with splats on BT surfaces having the lowest perimeter (392µm), whilst splats on ET and PT surfaces had larger, similar perimeters (~500µm). Thermal treatment had no effect on the B and BT surface pair, and the high scatter in the data makes it unlikely thermal treatment had any affects on the E and ET pair, but there was a significant increase in perimeter (50%) with thermal treatment of the P surface to a PT condition. At 323°C there was minimal difference between the six different pretreatments (~185µm). As expected the splat perimeters followed the trends of splat area, such that a large decrease occurred with increasing substrate temperature.

Due to the high scatter of area and perimeter on E and P surfaces it was considered that B, E and P surfaces actually resulted in no significant difference in splat perimeter. There was a difference in splat perimeter between P and PT surfaces at 23°C, with PT surfaces generating larger perimeter splats. This could be the result of increased magnesium on PT substrates in comparison with P substrates, but as B substrates presented a similar perimeter and had no magnesium present, it is likely that this result is a statistical anomaly, or at least, could not be explained by the variables analysed in this work. As with splat area, splat perimeters were much greater at 23°C than at 323°C, as a result of the recovery and crystallisation, as discussed in section 8.1.3.



Figure 8.8 Effect of surface pretreatment on the perimeter of HVAF sprayed PEEK splats.



Figure 8.9 Effect of surface pretreatment on the perimeter of HVAF sprayed PEEK splats on aluminium held at 323°C.

Trends with Treatment (constant Temp.)		Trends with Temp. (constant treatment)		
23°C	323°C	23°C		323°C
B~E~P	B~E~P	В	>	В
BT <et~pt< td=""><td>BT~ET~PT</td><td>E</td><td>></td><td>E</td></et~pt<>	BT~ET~PT	E	>	E
Thermal vs. Non-Thermal treatment		Р	>	Р
(constan	nt Temp.)	BT	>	BT
23°C	323°C	ET	>	ET
B~BT	B~BT	PT	>	PT
E~ET	E~ET			
P <pt< td=""><td>P~PT</td><td></td><td></td><td></td></pt<>	P~PT			

Table 8.4	Summary	of HVAF	"splat	perimeter"	results.
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8.1.5 Splat Feret diameter

The effect of pretreatment on splat Feret diameters followed the same trends as for splat area. At 23°C there was no difference in the Feret diameter of splats for any of the six substrates, nor was there any significant difference between the thermal treatment pairs of B and BT, E and ET or P and PT, all substrates resulting in splats about 85µm diameter. Substrates at 323°C were the same, with no difference in Feret diameter for any of the six pretreatments, and no significant difference between the thermal treatment pairs of B and BT, E and ET or P and PT, all substrates resulting in splats about 55µm diameter. Again the one significant difference was the decrease in diameter that occurred when the substrate temperature was raised to 323°C.

The results for Feret diameters of splats corroborated the splat area and splat perimeter results. The large decrease in diameter with increasing substrate temperature is explained in section 8.1.3.



Figure 8.10 Effect of surface pretreatment on the Feret diameter of HVAF sprayed PEEK splats.

Trends with Treatment (constant Temp.)		Trends with Temp. (constant treatment)		
23°C	323°C	23°C		323°C
B~E~P	B~E~P	В	>	В
BT~ET~PT	BT~ET~PT	E	>	E
Thermal vs. Non-Thermal treatment		Р	>	Р
(constan	t Temp.)	BT	>	BT
23°C	323°C	ET	>	ET
B~BT	B~BT	PT	>	PT
E~ET E~ET				
P~PT	P~PT			

Table 8.5	Summary	v of HVAF "s	splat Feret	diameter"	results
		,			

8.2 The effect of substrate temperature on HVAF splat properties

To evaluate the effect of substrate temperature on the properties of HVAF sprayed PEEK splats, the substrates were heated to the same temperatures as they were heated to for the plasma spray experiments.

Splat area, perimeter, and Feret diameter all followed the same trend, as could be expected. Area, perimeter and Feret diameter remained essentially constant between 23°C and 123°C, there was then a decrease in these values between 123°C and 163°C. Between 163°C and 363°C the area, perimeter and diameter again remained essentially constant. This trend is presented in Figure 8.11, Figure 8.12, and Figure 8.13. This trend was continued to splat circularity, but with a broader envelope above 143°C, shown in Figure 8.14. It is possible that circularity must be split into three groups, substrates below 143°C, substrates between 143°C and below 275°C and substrates at 275°C and greater. Substrates above 143°C needed to be split in two because at 275°C the kinetic energy transferred to thermal energy upon impact resulted in melting of the particles. Thus, splats on substrates 230°C and below all exhibited solid state spreading, whereas splats on substrates 275°C resulted in molten PEEK, which brought a new set of parameters into the equation. Kinetic energy conversion to thermal energy upon impact is discussed in detail in section 8.3.



Figure 8.11 Effect of substrate temperature on the area of HVAF sprayed PEEK single splats.



Figure 8.12 Effect of substrate temperature on the perimeter of HVAF sprayed PEEK single splats.



Figure 8.13 Effect of substrate temperature on the Feret diameter of HVAF sprayed PEEK splats.



Figure 8.14 Effect of substrate temperature on circularity of HVAF sprayed PEEK single splats.



As shown in the previous figures there was a distinct trend with temperature in splat area, perimeter and Feret diameter, where the results exhibited a step decrease between 123°C and 163°C. This temperature change covered the glass transition temperature of PEEK (143°C) and the two temperatures were chosen so that they bracketed the glass transition temperature of PEEK. The decrease was due to the different processes that occurred after impact on substrates above and below the glass transition temperature. On substrates below the glass transition temperature a particle will impact, spread, and then quench to a temperature near the substrate temperature, resulting in an amorphous splat. Particles impacting a substrate above the glass transition temperature will impact, spread, quench to near the substrate temperature, then slowly cool with the substrate through the glass transition. This allowed the splats to relax, recover any viscous-elastic strain to an equilibrium condition, and recrystallise through the glass transition temperature with the associated decrease in specific volume, resulting in splats of smaller area, perimeter and Feret diameter. The density of amorphous PEEK is 1260kgm⁻³, compared to 1320kgm⁻³ for crystalline PEEK, as per Table 2.2. That equates to a 4.5% reduction in specific volume when changing from amorphous PEEK to crystalline PEEK as a splat cools slowly through T_a. Assuming an essentially two dimensional splat, a 4.5% volume reduction will translate to a 4.5% areal reduction. The results of HVAF sprayed PEEK splats sprayed on substrates heated to 163°C and above exhibited a decrease in area of about 35%. Such a large decrease in area can not solely be due to the difference between crystalline and amorphous PEEK specific volumes, and recovery of visco-elastic residual stress and strain within splats deposited on substrates 163°C and hotter is suggested as the mechanism for this decrease. Crystallinity of the splats was not measured due to the difficulty in collecting a large enough sample of single splats to be tested by either differential scanning calorimetry, x-ray diffraction or thermogravimetric analysis. Sprayed coatings would have been much easier to test the crystallinity of compared to single splats, but neither the facilities to generate coatings nor the facilities to analyse the crystallinity of single splats were available.

A similar decrease in splat area with increasing substrate temperature (as was seen with the HVAF sprayed PEEK splats) was reported by MacDonald et al. [87] who reported molybdenum splats deposited on heated glass substrates (400°C) by plasma spray spreading to a lesser degree, thought to be due to improved contact with the substrate resulting in faster cooling of the splats. Due to the significant differences of the thermal properties of molybdenum and PEEK splats and cooling rates of polymer splats being orders of magnitude slower than metal splats, with polymer splats typically completely spread before significant cooling occurs due to the low thermal conductivity of polymers 111 [56, 60], it is thought that the T_g of PEEK played a significant role in the area of PEEK splats, whilst acknowledging that increased splat cooling rates will also partially contribute to reduced splat spreading.

Something not shown in the graphs, but depicted in Figure 8.15, was the degree of melting of splats, which can only be qualitatively analysed through inspection of the SEM images. Analysis of these images showed that splats on room temperature substrates, and on substrates up to 230°C, did not appear to have melted and have instead impacted in a solid or semi-solid state. Image analysis of the splats on substrates with increasing temperature revealed that substrates held at 275°C resulted in molten splats. As lower



Figure 8.15 The change in HVAF splats with increasing substrate temperature

temperature substrates showed that splats were not molten in flight, this showed that the combination of the kinetic energy of the particle and the increased substrate temperature result in post impact melting of the PEEK particles, as discussed in section 8.3. As the substrate was 68°C below the melting temperature of PEEK, this was evidence that the change of kinetic energy to thermal energy on impact of thermal spray particles could add significant thermal energy to a system, and in the case of the spray conditions used in these experiments, it was a great enough increase to result in molten splats as opposed to the solid or semi-solid splats that were imaged on substrates held at temperatures up to and including 230°C.

8.3 Kinetic energy conversion to thermal energy on particle impact

As has been mentioned in sections 7.2, 8.1, and 8.2 splats deposited on substrates heated to 323°C have exhibited melting. In the case of plasma sprayed splats, the splats appeared significantly more molten on 323°C substrates than they did on lower temperature substrates. Note, the melting point of PEEK is 343°C. For HVAF sprayed splats, splats deposited on room temperature substrates (and substrates heated up to 230°C) appeared to have been solid or highly viscous on impact, whilst splats deposited on substrates heated to temperatures of 275°C and higher appeared molten. This is important as 275°C is 68°C below the melting point of the PEEK powder, and the HVAF particles were shown to not be molten in flight. It is proposed that the additional thermal energy required to melt the PEEK particles on impact was the result of the conversion of the kinetic energy of the particles to thermal energy upon impact.

The kinetic energy of sprayed particles in flight will be converted into the kinetic energy of the particle spreading across the substrate, the energy required to deform the particle and thermal energy. The kinetic energy of sprayed particles can be determined according to equation 8-1:

Equation 8-1 $KE = 0.5mv^2$

KE = Kinetic energy

m = mass

v = velocity

The portion of the kinetic energy that is converted into thermal energy will raise the temperature of the particle. The thermal energy required to raise the temperature of an object by a given temperature can be determined with equation 8-2:

Equation 8-2 $\Delta T = \frac{\Delta H}{mc_p}$

- ΔH = change in thermal energy
- *m* = mass
- c_p = heat capacity
- ΔT = change in temperature

To calculate the temperature rise in a particle upon impact, equation 8-1 and 8-2 can be combined as follows to form equation 8-3:

$$\Delta T = \frac{k\Delta H}{mc_p}$$
$$\Delta T = \frac{k.0.5mv^2}{mc_p}$$

Equation 8-3 $\Delta T = \frac{0.5kv^2}{c_p}$

k = a constant determining the fraction of kinetic energy converted to thermal energy

As can be seen from equation 8-3, the mass of a particle cancels out, and the temperature rise of any particle can be determined from the fraction of kinetic energy that converts to thermal energy, the velocity of the particle, and the heat capacity of the particle. The heat capacity of PEEK is 2200J.kg⁻¹.°C⁻¹, as per Table 2.2. Plotting the potential temperature increase from a given particle velocity allowed the two spray processes to be compared, shown in Figure 8.16. Plasma sprayed particles, which typically have velocities in the range of 200ms⁻¹ to 400ms⁻¹, could have had a temperature increase of between 10°C and 30°C. In contrast, HVAF sprayed particles, which typically have velocities in the range of 500ms⁻¹ to 650ms⁻¹, could have had a temperature increase of 40°C to 80°C. Particle velocities are always a distribution, with heavier particles travelling more slowly and lighter particles achieving higher velocities. As PEEK powder had a lower density than most metals and ceramics, it is reasonable to expect that PEEK particle velocities were at the upper end of the typical velocity ranges of the respective thermal spray processes.

Based on the calculations of temperature increases for the assumed particle velocities of the two thermal spray processes, plasma and HVAF, it was reasonable to believe that plasma sprayed particles deposited on substrates heated to 323°C could receive enough



Figure 8.16 Particle temperature increase for different particle velocities with different fractional conversion of kinetic energy to thermal energy.

thermal energy to show increased melting of these particles after impact. Similarly, particles sprayed by HVAF and deposited on substrates heated to 275°C can reasonably be expected to have been heated to a great enough extent to reach the 343°C melting temperature of PEEK.

8.4 HVAF discussion summary

The number of splats deposited by HVAF spraying was not affected by surface chemistry when the substrates were at room temperature or at 323°C. Substrates held at 323°C during spraying, however, showed a strong sensitivity to surface morphology, with the number of splats deposited increasing with decreasing surface roughness. Splat circularity was affected by surface chemistry on substrates at room temperature, but for substrates at 323°C, the determining factor again appeared to be the surface morphology of the substrate. The most significant result was the large increase in circularity associated with increasing substrate temperature from ambient to 323°C. Splat area was unaffected by surface chemistry at both ambient and 323°C, but at 323°C, splat area was affected by surface morphology, with the smoother surfaces resulting in larger splats. Substrate temperature, however, had the greatest effect on splat area, with an increase in substrate temperature resulting in a dramatic decrease in splat area. Splat perimeter and Feret diameter were unaffected by surface chemistry or morphology at either room temperature or 323°C, but showed the same trend with substrate temperature as splat area with dramatically lower values on substrates held at 323°C.

As mentioned above, substrate temperature had a significant effect on splat properties. This finding was reinforced by the substrate temperature trials, which revealed a significant step in the results, corresponding to greater circularity, and lower splat area, perimeter and Feret diameter. This step occurred between 123°C and 163°C, the two temperatures bracketing the glass transition temperature of PEEK (143°C). These results were due to splats on substrates above T_g cooling slowly with the substrate through T_g and allowing crystallisation to occur, whilst those sprayed onto substrates below T_g quench through T_g resulting in amorphous splats. Splats sprayed onto substrates above T_g will also cool more slowly, allowing them to "relax" and recover any elastic strain caused by the impact. The difference in results between plasma spray and HVAF was a result of this elastic relaxation of the splats, with HVAF deposited splats having a much greater magnitude of strain due to the much higher impact velocity associated with HVAF spraying. Plasma sprayed splats will also be in a more liquid condition upon impact due to their longer flight in a higher temperature environment, reducing the visco-elastic properties of the plasma particles on impact.

9 Mechanism of Splat Formation

There are four distinct time periods important to the formation of thermal spray coatings, the period the particles are in flight, the moment of impact, spreading across the surface and post impact effects, as depicted in Figure 9.1.



Figure 9.1 The four stages of splat deposition which can affect splat properties. In flight, impact, spreading, and post impact affects.

9.1 Particles in Flight

The in-flight period, period 1 in Figure 9.1, is when heat is transferred to the particle from the thermal spray torch. The thermal spray plume can be characterised by its temperature, velocity, and gas composition. The hotter the thermal spray flame plume, the greater the driving force for heat transfer to the particle. The faster the plume, the greater the velocity of the particle, and the shorter the residence time of the particle in the plume, affecting the time available for heat transfer. The plasma plume used in this research was hot and had a moderate velocity (temperature ~2500°C, particle velocities 300 – 400ms⁻¹, numbers extrapolated from Sampath et al. [112]), whilst the HVAF flame was cool and had a high velocity (temperature $\sim 1200^{\circ}$ C, particle velocities 500 – 700ms⁻¹, numbers extracted from Browning [55]). The result of this was that PEEK particles in the plasma plume had a high degree of heat transfer for a moderate length residence time, and appeared to have reached a molten but viscous condition, and been accelerated to a velocity of 300 to 400ms⁻¹. PEEK particles in the HVAF flame reached a high velocity (500 to 700ms⁻¹) and appeared to have only had a low degree of heat transfer during a short residence time, with only an outer layer becoming molten, whilst the centre of the particles remained solid. Thus the two spray systems resulted in very different particle properties upon impact.

Polymer splats have been reported as having a "fried-egg" morphology, as shown schematically in Figure 9.2, thought to be the result of steep temperature gradients through polymer particles and thus a viscosity gradient with a low viscosity outer layer

and a high viscosity core resulting in splats that resemble a fried-egg with the yolk in the centre [56, 65]. The plasma sprayed PEEK in this work did not form fried-egg splats, most likely due to the outer layers still having a high viscosity in comparison to the nylon 11 particles that formed fried-egg splats. The plasma sprayed splats were similar to the flame sprayed UHMWPE splats deposited by Bao et al. [91] suggesting similar particle viscosity profiles in flight. In contrast the high thermal conductivities of metal particles result in a uniform temperature throughout the particle [61]. Ceramic powders do not have the high thermal conductivity of metals, but their very high thermal degradation temperatures allow the use of high temperature plasma plumes that provide a high driving force for heat transfer and result in molten ceramic particles [61]. The low thermal degradation temperatures of polymers prevent this technique being used to achieve completely molten polymer particles.

HVAF sprayed PEEK splats did not appear to be fully molten on impact, so whilst they probably had a temperature profile as shown in Figure 9.2, only a very thin layer, if any, of the particle was molten, and the particles ruptured on impact.

9.2 Particle Impact

Upon impact of a particle with a substrate the viscosity and velocity of the particle, in combination with the condition of the substrate, determine the degree of intimate contact between the particle and the substrate. The kinetic energy of the particle will also need to change, some kinetic energy will be translated into the perpendicular direction, spreading the splat across the surface, some will be absorbed in the work of deforming the particle, and some will be absorbed as heat energy, heating the particle.

To achieve a high degree of intimate contact with a substrate, a particle must have a sufficiently low viscosity or a significantly high velocity or a combination of the two. Substrate variables that affect the degree of intimate contact a particle has with the substrate are surface roughness and the temperature at which the substrate will degas, as depicted in Figure 9.3. Degassing is either a result of hydroxide dehydration, or the boiling off of adsorbates on the surface, and is caused by a combination of the thermal energy of the thermal spray torch and the thermal energy of the particle upon impact.



Figure 9.2 Schematic of a particle in flight (the lighter the shade, the higher the temperature) and the resultant "fried egg" splat formation.



Figure 9.3 Degree of intimate contact can be decreased by substrate degassing (A) or by inability of a particle to flow into surface features (B).

The lower the degree of intimate surface contact the slower the heat transfer between the particle and the substrate and the lower the adhesion of the particle to the substrate due to the reduced bonding area (irrespective of whether it is due to chemical bonding or due to mechanical interlocking).

In this research the plasma sprayed PEEK splats appeared to have been molten and at moderate velocity on impact, and evidence of significant degassing of B and BT substrates due to plasma plume thermal energy was presented in section 7.3. HVAF sprayed PEEK splats appeared to have only had a thin molten layer on impact, but to have impacted at high velocity. B and BT substrates that were HVAF sprayed also showed evidence of degassing due to thermal energy from the HVAF flame, but the degassing was not as great as for the plasma sprayed substrates. Splats from both processes are likely to have suffered reduced intimate contact on the B and BT substrates due to degassing, but more so for the plasma sprayed splats. Degassing would have occurred on all substrates with chemisorbed water present (B, BT, E), but the physical evidence was only present on the B and BT substrates. Plasma sprayed splats are likely to have had higher intimate contact with the E and ET substrates due to the

lower viscosity on impact, compared to the HVAF sprayed PEEK particles which appeared to have been essentially solid on impact, so were unlikely to have conformed to the rough substrate, despite the high velocities.

In contrast to polymer particles, metals have significantly lower viscosities when molten (1 – 10mPa.s [113]), giving metal particles a better chance of achieving a high degree of intimate contact with a rough substrate. Degassing of substrates is known to increase porosity and splat splashing and decrease the degree of intimate contact of metal and ceramic splats on a substrate [58, 61]. Low viscosity polymers such as nylon-11 (10-50Pa.s [56]) on a heated substrate may conform to the substrate resulting in a high degree of intimate contact, and adhesion studies showing increased adhesion with increased substrate temperature suggest the degree of intimate contact does increase with substrate temperature for nylon-11 particles [56].

9.3 Splat Spreading

Splat spreading is essentially affected by the same parameters as particle impact, but these parameters have different effects on the spreading of splats across the substrate surface.

Substrate roughness affects the way a splat flows across the surface, with rough surfaces resulting in jetting and fingering of splats due to unstable flow conditions. Degassing of a substrate is also likely to destabilise the flow of a splat across the surface as gas released by thermal energy transfer to the substrate tries to leave the substrate. Surface chemistry possibly has an effect on the spreading of a splat, as different surfaces will have different wetting angles with respect to the spreading particle, with surfaces with lower wetting angles providing less resistance to spreading than a surface with a high wetting angle.

Plasma splats with their molten viscous state were observed to spread further to form larger splats on surfaces that had less chemisorbed water, and therefore less tendency to degas, they also formed larger splats on the P and PT surfaces, especially on 323°C substrates. Plasma splats were also found to be more circular on E, ET, P and PT substrates at room temperature than those on B and BT substrates. This was likely a result of the significant degassing of the B and BT substrates. The high surface roughness of the E and ET substrates did not affect the circularity of the splats significantly, probably due to the viscosity of the PEEK suppressing jetting and fingering.

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HVAF splats on room temperature substrates were not molten and appeared to have torn apart on impact, as such, the form of the splats was predominantly due to the velocity of the particle in flight and its rupture on impact. Particles impacting a 323°C substrate appeared molten, but that was likely a post impact effect, as will be discussed below.

The significantly different viscosities of thermally sprayed polymer and metal particles result in different spreading effects. Both metal and polymer splats are less circular (more fingered) when sprayed on room temperature substrates than when sprayed on heated substrates [56, 58, 61, 81, 90]. The significant difference is the degree of fingering of a metal splat, which is much greater than that of polymer splats, due to the lower viscosity of the splat. Condensates on the surface and surface roughness have both been shown to reduce the circularity of metal and ceramic splats [58, 61, 90], as they do for plasma sprayed PEEK splats and HVOF sprayed nylon-11 splats [56, 65]. HVAF sprayed PEEK splats appear to have spread due to particle rupture upon impact, as opposed to flow of material across the substrate, and as such do not follow the same trends as plasma sprayed PEEK splats.

9.4 Post Impact Effects

Polymer splats, due to their low thermal conductivity, have a low transfer rate of heat to the substrate resulting in the completion of spreading $(1-5\mu s [53])$ well before splat solidification begins (1-5m s [53]). In contrast, metal particles cool at a similar timescale $(3-10\mu s [61])$ to the spreading of a splat $(1-5\mu s [61])$ and as such splat spreading is affected by splat solidification. Furthermore it has been shown that splats on a heated substrate cool an order of magnitude more slowly than splats deposited on a room temperature substrate [56, 65]. The rate of heat transfer is not only affected by the driving force, but by the degree of intimate contact controlling the available area for heat transfer, and the thickness of the oxide layer which will have a lower thermal conductivity than the substrate.

Both plasma and HVAF sprayed splats showed signs of post impact melting on 323°C substrates, 20°C below the melting point of PEEK, with HVAF splats also showing post impact melting on substrates at 275°C, nearly 70°C below the melting point of PEEK. It is suggested that this post impact melting was the result of the conversion of kinetic energy upon impact to thermal energy, which due to the elevated substrate temperature dissipated slowly from the splat, and provided sufficient energy to melt the PEEK particle. This was not observed at lower temperatures, due to the faster dissipation of heat energy to the substrate. The HVAF sprayed particles, although essentially solid in flight, 121

possessed much higher kinetic energy resulting in a greater thermal energy upon impact. The post impact melting resulted in significantly more circular splats than on room temperature substrates. The plasma particles appeared to become molten but highly viscous in flight, and post impact melting on high temperature substrates resulted in more circular splats, although no increase in area.

The circularity of HVAF sprayed splats on E and ET substrates was lower than the smoother P, PT, B and BT substrates. This was due to the resistance to flow of the rough E and ET surfaces reducing the ability of post impact splat melting to fill in the gaps between the fingers resulting from the particle rupture upon impact.

Unexpectedly, HVAF sprayed splats were found to have significantly smaller areas when deposited on substrates heated to 163°C and higher. This was thought to be due to the slowed heat transfer from the particle to allow the particles to relax any residual viscoelastic strain resulting from the impact. This phenomenon was not seen in the plasma sprayed splats due to the lower impact velocities and the more molten nature of the particles upon impact, essentially resulting in less strain and the ability to recover what strain is imparted.

Splats deposited on heated substrates will, after enough time, reach the same temperature as the substrate, then cool with the substrate back to room temperature. This means that splats deposited on substrates heated above the glass transition temperature of PEEK (143°C) will cool slowly through the glass transition temperature, forming crystalline or semi-crystalline splats. Whilst those deposited on substrates below the glass transition temperature will quench to the substrate temperature, likely forming amorphous splats (depending on the natural cooling rate). Although no evidence of the crystallinity of splats has been observed it must be considered. The crystalline form of PEEK has a lower specific volume than amorphous PEEK, but the difference is well within the experimental variability of these experiments for definitive observations to be made.

The HVAF sprayed PEEK splats deposited on substrates heated to 275°C and hotter, and the plasma sprayed PEEK splats deposited on substrates at 323°C and hotter compared well with HVOF sprayed nylon-11 splats deposited on substrates heated to 190°C (above the ~170°C melting point of nylon-11) [56, 65]. Nylon-11 splats deposited on heated substrates also reduced in size and increased in circularity due to post impact recovery of residual stress/strain and/or visco-elastic effects [56, 65], in a similar way to

both the HVAF and plasma sprayed PEEK splats. The key factor is that the HVAF splats exhibited this on substrates ~70°C below the melting point of PEEK, and plasma sprayed splats exhibited this trend on substrates 20°C below the melting point of PEEK. HVAF splat shrinkage was even exhibited at substrate temperatures as low as 163°C, but melting was only observed at 275°C and above.

As can be seen, the morphology of a thermally sprayed particle was dependent on a wide range of variables, including the spray technique, the particles' physical and thermodynamic properties, and the substrate conditions. The final form of a splat was determined by the variables that are dominant in any one thermal spray system. In the HVAF spraying of PEEK, particle temperature, particle velocity and substrate temperature are the three primary variables that determine the form of the PEEK splats. In the plasma spraying of PEEK, particle temperature, particle velocity, substrate temperature <u>and substrate surface conditions</u>, including the degree of adsorbates, degassing of the substrate and substrate roughness, can be considered the variables that determine the form of the PEEK splats.

10 Conclusions

When plasma spraying, the surface chemistry of the substrate has been shown to have a significant effect on the number of splats deposited on a substrate. It was found that decreasing the amount of hydroxide and chemisorbed water on a substrate surface resulted in an increase in the number of splats deposited by plasma spraying.

The amount of hydroxide and chemisorbed water present on the substrate surfaces also affected the circularity and area of plasma sprayed splats, with low levels of hydroxide resulting in splats of greater circularity and greater area.

Thermal treatment of the surfaces only had a significant effect on the boehmitic and thermally treated boehmitic pair (B and BT), where thermal treatment resulted in increased circularity and an increased number of plasma sprayed splats on substrates held at 23°C.

Substrate temperature had a minimal effect on plasma sprayed splats in the measurable properties, although splat appearance did change with increasing substrate temperature, due in part to recrystallisation of splats on cooling and in part to melting of splats after impact.

When HVAF spraying, surface chemistry did affect the circularity of splats sprayed onto a room temperature substrate, with decreasing amounts of hydroxide and chemisorbed water on the surface leading to increased circularity. However, the surface chemistry of the substrate did not affect the number of splats deposited by HVAF, the area, perimeter or Feret diameter of those splats deposited on room temperature substrates.

For substrates held at 323°C, surface morphology/roughness dominated HVAF sprayed splat properties. The smoother the surface, the more splats were deposited on the substrate. Splat area and circularity followed the same trend, with smoother surfaces resulting in more circular splats of greater area.

The most significant result of the HVAF spray trials was the significant decrease in area of splats on all substrate pretreatments with a corresponding decrease in perimeter and diameter as well as an increase in circularity when substrates were heated to 323°C from 23°C.

The above result was mirrored in the surface temperature trials on polished substrates, which revealed that a decrease in HVAF sprayed splat area occurred as a step between 123°C and 163°C. This corresponded with the step over the glass transition temperature. It is thought that as the splats cool slowly through the glass transition temperature with the substrate the splats relax, crystallise, and shrink. Splats deposited on substrates below the glass transition temperature quenched to form amorphous splats that did not shrink. This trend was not evident in the plasma system due to the lower velocities resulting in less residual strain in the splats.

To achieve splats of high circularity which are molten on impact, polished substrates were shown to be the best substrate for both HVAF and plasma spraying. Plasma spraying required the preheating of the substrate to 323°C, whilst HVAF spraying only required preheating to 275°C. Plasma spraying appeared to degrade to outer layer of PEEK splats, so HVAF spraying is recommended for the formation of PEEK coatings over plasma spraying. Note these recommendations do not take into account adhesion of PEEK to the substrate, where the rough etched substrate surface is likely to perform better than the polished substrate in adhesion tests.

This study has proven that substrate surface chemistry can have a significant effect on the properties of single PEEK splats deposited on a surface. Surface chemistry can be altered by thermal or chemical treatment, and can be tailored to provide optimised conditions for adhesion of a coating, which is dependent on the initial layer of splats deposited on the surface. The thermal spray industry takes great care to prepare surface morphology before coating, this study shows that as much care should be placed on preparing the surface chemistry before coating.

This study has also provided proof that the kinetic energy of particles on impact provides enough thermal energy to raise the temperature of PEEK particles on the order of 60°C, into the less viscous region, allowing for improved splat properties. This will allow closer tolerances to be investigated for the thermal spraying of polymers, and the kinetic energy to be utilised with a reduction of thermal energy such that thermal degradation of polymers can be minimised.

Whilst this work has answered many questions, as with all research, there are yet more questions to be answered. Work to characterise the crystallinity of PEEK single splats sprayed by the two processes should be performed such that the influence of T_g on HVAF

sprayed splat properties can be quantitatively assessed. Directly following on from this work would be the formation of thermally sprayed PEEK coatings on the substrate set tested in this work and the testing of adhesion, barrier properties (corrosion resistance), and crystallinity of PEEK coatings.

To further investigate the effect that substrate surface chemistry had on single splat morphology, spraying of metal powders onto the same substrate set PEEK was deposited on would help differentiate surface chemistry effects from those effects that resulted from the polymer particle properties.

11 References

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Appendix A

Plasma circularity distributions



Plasma B 23°C Circularity distribution



Plasma B 323°C Circularity distribution



Plasma BT 23°C Circularity distribution



Plasma BT 323°C Circularity distribution



Plasma E 23°C Circularity distribution



Plasma E 323°C Circularity distribution



Plasma ET 23°C Circularity distribution



Plasma ET 323°C Circularity distribution


Plasma P 23°C Circularity distribution



Plasma P 323°C Circularity distribution



Plasma PT 23°C Circularity distribution



Plasma PT 323°C Circularity distribution

HVAF circularity distributions



HVAF B 23°C Circularity distribution



HVAF 323°C Circularity distribution







HVAF BT 323°C Circularity distribution



HVAF E 23°C Circularity distribution







HVAF ET 23°C Circularity distribution









HVAF P 23°C Circularity distribution



HVAF P 323°C Circularity distribution



HVAF PT 23°C Circularity distribution



HVAF PT 323°C Circularity distribution

Appendix B



Plasma splat area distributions

Plasma B 23°C splat area distribution



Plasma B 323°C splat area distribution



Plasma BT 23°C splat area distribution



Plasma BT 323°C splat area distribution



Plasma E 23°C splat area distribution







Plasma ET 23°C splat area distribution



Plasma ET 323°C splat area distribution







Plasma P 323°C splat area distribution



Plasma PT 23°C splat area distribution



Plasma PT 323°C splat area distribution



HVAF B 23°C splat area distribution



HVAF B 323°C splat area distribution







HVAF BT 323°C splat area distribution



HVAF E 23°C splat area distribution







HVAF ET 23°C splat area distribution













HVAF P 323°C splat area distribution



HVAF PT 23°C splat area distribution



HVAF PT 323°C splat area distribution