JTTEE5 17:631–636
DOI: 10.1007/s11666-008-9250-9
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The Effect of Surface Chemistry and Morphology on the Properties of HVAF PEEK Single Splats

B.P. Withy, M.M. Hyland, and B.J. James

(Submitted April 28, 2008; in revised form August 3, 2008)

Thermal spray of polymers has had limited investigation due to the narrow processing windows that are inherent to polymer powders, especially their low temperatures of thermal degradation. The polymer poly aryl ether ether ketone (PEEK) has a continuous use temperature of 260 °C, does not suffer significant thermal degradation below 500 °C (Lu et al., Polymer, 37(14):2999-3009, 1996), and has high resistance to alkaline and acidic attack. These properties led to PEEK being selected for investigation. To minimize thermal degradation of the particles, the high velocity air fuel technique was used. To investigate the effect of substrate pretreatment on single splat properties, single splats were collected on aluminum 5052 substrates with six different pretreatments. The single splats collected were imaged by scanning electron microscopy and image analysis was performed with ImageJ, an open source scientific graphics package. On substrates held at 323 °C, it was found that substrate pretreatment had a significant effect on the circularity and area of single splats, and also on the number of splats deposited on the substrates. Increases in splat circularity, area, and the number of splats deposited on the surface were linked to the decrease in chemisorbed water on the substrate surface and the decrease of surface roughness. This proved that surface chemistry and roughness are crucial to forming single splats with good properties, which will lead to coatings of good properties.

Keywords coating-substrate interaction, HVAF, influence of process parameters, polymer, single splats

1. Introduction

Poly aryl ether ether ketone (PEEK) is a polymer that can be used to form wear- and corrosion-resistant coatings. It is also a food safe polymer that makes it ideal for coatings in the food processing industry. PEEK is a highly stable polymer and suffers no chemical attack by water and steam. It 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 to 300 °C (Ref 1). 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 PEEK will not suffer degradation during the high-temperature alkali- or acid-cleaning regimes (Ref 2). PEEK has a low coefficient of friction compared to most metals and ceramics and good wear resistance compared to other polymers (Ref 3); in combination with its chemical resistance this makes PEEK suitable for use for components in pumps and other high-pressure, wear-sensitive situations. A summary of the physical properties of PEEK is shown in Table 1.

In high velocity air fuel (HVAF) thermal spraying, compressed air is used as the combustion agent. The presence of nitrogen in the combustion gases results in HVAF guns having a cooler, less-oxidizing flame than high velocity oxygen fuel (HVOF) guns, which should result in less thermal degradation of polymer particles (Ref 4). Typically an HVOF system has a flame temperature of approximately 2650 °C, while the Browning HVAF system has a flame temperature of approximately 1870 °C (Ref 5). Particle velocities of the HVAF system are also typically lower than those of HVOF systems, which at a combustion chamber pressure of 0.4 MPa are about 600 and 800 ms^{-1}, respectively (Ref 5).

The interaction of thermal spray particles with the substrate upon impact has predominantly focused on metallic and ceramic particles. Studies have shown that room temperature substrates result in fingered splats, while heating the substrate results in a higher proportion of disc splats (Ref 6-9). Surface roughness has also been

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This article is an invited paper selected from presentations at the 2008 International Thermal Spray Conference and has been expanded from the original presentation. It is simultaneously published in *Thermal Spray Crossing Borders, Proceedings of the 2008 International Thermal Spray Conference*, Maastricht, The Netherlands, June 2-4, 2008, Basil R. Marple, Margaret M. Hyland, Yuk-Chiu Lau, Chang-Jiu Li, Rogerio S. Lima, and Ghislain Montavon, Ed., ASM International, Materials Park, OH, 2008.

B.P. Withy, Applied Vehicle Systems, Defence Technology Agency, Auckland, New Zealand; and **M.M. Hyland** and **B.J. James**, Chemical and Materials Engineering, University of Auckland, Auckland, New Zealand. Contact e-mail: b.withy@dta.mil.nz.

shown to have an effect, with rough surfaces resulting in increased fingering of splats (Ref 6, 8). If the interactions can be optimized to produce disc splats with intimate contact between splat and substrate, coatings with improved adhesion and porosity should result. This study has approached the interaction of particles with the substrate by controlling substrate conditions and observing the resulting splats. Common splat forms for polymer splats include disc, 'fried egg,' and splashed or fingered morphologies (Ref 10, 11). Disc splats, of which 'fried egg' splats are a subgroup, tend to result in coatings with good adhesion and cohesion with low coating porosity, while conversely, coatings formed from splashed splats have high porosity and poor adhesion and cohesion (Ref 10-13). Polymer particles are usually sprayed in a semimolten state where the center of the particle remains solid while the outer layer melts due to the low thermal conductivity of polymers (Ref 11). Substrate temperature is also critical when spraying polymers, and whether it is above or below the glass transition temperature (T_g) and above or below the melting temperature (T_m) will have an effect on the splat and coating properties (Ref 10). Splats deposited on a substrate above the T_m can receive additional thermal energy from the substrate allowing a high degree of conformity with the substrate, similar to that achieved with fully molten particles. Substrates above the T_g that cool slowly after splat deposition tend to lead to semicrystalline coatings, and the coating stresses associated with change in specific volume of the polymer must be considered. Finally, polymers that are deposited on substrates below T_g, or which are quenched, form amorphous coatings with properties analogous to those of the amorphous polymer (Ref 10, 11, 14-17).

In this study, PEEK splats were deposited on substrates subjected to 6 different pretreatments to change the surface chemistry and morphology of the substrates. In a wider study a range of substrate temperatures during spraying was investigated, but the discussion here is restricted to splat formation on substrates held at a temperature between T_g and T_m during spraying. Splats on each substrate were characterized by the number of splats deposited on a given area of substrate (splat area density), the area of individual splats, and their circularity. Characterization of splats was carried out by image analysis of backscatter scanning electron microscopy images.

Table 1 Physical properties of PEEK 150PF as supplied by Victrex

Glass transition temperature (T_g)	143 °C
Melting temperature (T_m)	343 °C
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	
Above T_g	4.7×10^{-5} °C^{-1}
Below T_g	10.8×10^{-5} °C^{-1}

2. Experimental Procedure

Single splats of PEEK were collected on 20 mm square AA5052 substrates that had been pretreated by one of the six pretreatments and were held at 323 °C (below the T_m and above the T_g of PEEK). Substrates were mounted on a heated copper block whose temperature was monitored by two K-type thermocouples.

Six pretreatments were used to prepare the aluminum substrates, polished (P), polished and thermally treated (PT), etched (E), etched and thermally treated (ET), boiled (B), and boiled and thermally treated (BT). Substrates were received in the polished condition and degreased with acetone. Etching involved a 10 min etch in AcidBrite, a Henkel (Auckland, New Zealand) etchant composed of 15% HF and 10% H_2SO_4. Boiling involved immersion in boiling deionized water for 30 min to form a layer of aluminum oxyhydroxide (AlOOH) on the substrate surface. Thermal treatment was a 350 °C soak for 90 min to drive off organic adsorbates and adsorbed water from the substrates. The etching process removed the native oxide layer and replaced it with a thin hydrated oxide layer, boiling built up a thick layer of aluminum oxyhydroxide on top of the native oxide layer, and polishing removed the native oxide layer and allowed it to reform under controlled laboratory conditions. Thermal treatment of these substrates resulted in the dehydration of the oxide layers to varying extent, but did not form additional oxide. These pretreatments were selected for their effect on the oxide layer composition and their effect on surface roughness as discussed in the Results and Discussion and summarized in Table 2 and Fig. 1. Pretreated substrates of different oxide layer composition and similar roughness and, conversely, substrates of different roughnesses but similar chemistry were produced by these pretreatments, and thus the influence of surface roughness on single splat morphology could be differentiated from the influence of oxide layer composition.

Particles were sprayed with an HVAF Browning Aerospray 150 (Browning Thermal Systems Inc., Enfield, New Hampshire) with a 100 mm nozzle and 200 mm spray distance. These operating parameters were selected based on a simple optimization that considered three nozzles (50, 100, and 200 mm) and three spray distances (100, 200, and 300 mm). The 100 mm nozzle with a 200 mm spray distance was found to result in the greatest deposition efficiency. The Aerospray burns kerosene and compressed air to generate a high velocity flame through a barrel nozzle. The system generated a combustion chamber pressure of 0.4 MPa, which corresponds to a flame velocity of ~600 ms^{-1}; particle velocity and temperature could not

Table 2 Surface roughness measurements of the different surface pretreatments

	B	BT	E	ET	P	PT
R_a, nm	34	18	253	254	12	12
Skewness	−0.41	0.22	0.53	−0.21	−0.14	−0.14

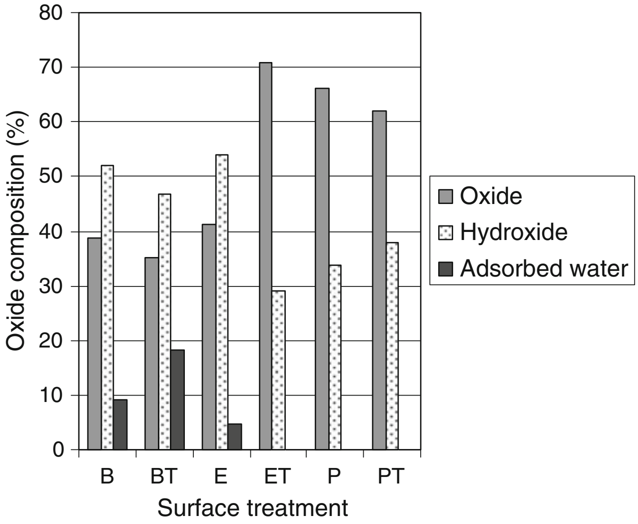

Fig. 1 Fraction of aluminum oxide, aluminum hydroxide, and chemisorbed water on substrate surfaces

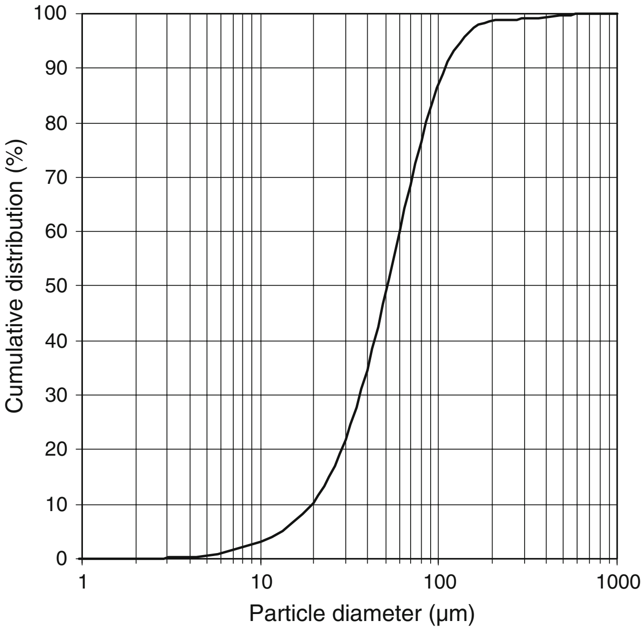

Fig. 2 Cumulative size distribution of PEEK feedstock powder

be measured with this system. Powder was fed at a rate of 7 g/min from a vibrating screw type powder feeder with nitrogen as the carrier gas. The feedstock had a nominal median diameter of 50 μm and a range of 0 to 100 μm, and a measured distribution as displayed in Fig. 2 . Single splats were achieved with a 0.5 ms^{-1} horizontal swipe across the substrates. Splats analyzed were from the center of the spray pattern.

The surface chemistry and roughness resulting from each pretreatment were determined by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (Digital Instruments NanoScope IIIa, Santa Barbara, CA), respectively. XPS (Kratos Ultra DLD, Manchester, UK) revealed the elemental composition of the substrate surface, the oxidation states of the aluminum oxide species, and the relative proportions of oxide, hydroxide, and adsorbed water. This technique is extremely surface-sensitive, analyzing only the outermost 5 nm of the surface.

Splats were imaged using a FEI Quanta 200 FEG environmental scanning electron microscope (Hillsboro, OR), utilizing backscatter imaging to provide improved definition between polymer splats and aluminum substrates. Image analysis was performed with the open source software ImageJ (Ref 18), which enabled splat counting, measurement of splat area, and circularity. Five images of each substrate (from the area in the center of the spray pattern) were analyzed, with each image containing at least 50 splats of area greater than 200 μm^2. Splats smaller than 200 μm^2 were not counted as they were determined to be the result of splashing, and not primary splats. The area of a splat was computed by summing the number of pixels in a splat and multiplying by the area of a single pixel as defined by the scale. Circularity is calculated by the formula $4\pi A/(\text{perimeter}^2)$, 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 the splat.

3. Results and Discussion

The six pretreatments resulted in different surface roughnesses as listed in Table 2. Surface roughness was measured over a 50 μm square area, the typical interaction area of a PEEK splat in this study. Boiling resulted in a slight increase in roughness over the polished surfaces, while the etching resulted in a very rough surface. The thermal treatment had little or no effect on the substrate surface roughness.

The oxide layer present on the surface of aluminum is a combination of various alumina phases, from aluminum trihydroxide ($Al(OH)_3$), to aluminum oxyhydroxide (ALOOH) to transition aluminas and corundum (Al_2O_3) (Ref 19, 20). This results in three resolvable oxygen components in the 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 (Ref 21). The six pretreatments used result in different ratios of oxide, hydroxide, and chemisorbed water on the aluminum substrate surfaces, as shown in Fig. 1. The surface of P and PT substrates are dominated by oxide, with some hydroxide from the reaction with atmospheric moisture, while E and ET surfaces have a higher proportion of hydroxide to oxide. These oxide layers are very thin, approximately 4 nm, compared to 225 nm for the B and BT oxide layers. While the boiled surface appears to have a similar surface chemistry to that of E, it is in fact quite a thick oxyhydroxide. This is evidenced in the thermal treatments when the very thin etched oxide rapidly loses its surface hydroxide, whereas the thicker boiled sample changes very little, because the oxide is so thick. The increase in chemisorbed water on the BT surface is due to a thin surface layer of aluminum oxyhydroxide dehydrating with the heat energy of thermal treatment. This then adsorbs atmospheric moisture increasing the chemisorbed water content of the surface relative to the B surface. Dehydration starts to occur at temperatures above 300 °C according to the reaction (Ref 20):

$$2\text{AlOOH} \rightarrow \gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O}$$

The change in hydroxide concentration on the etched surfaces with thermal treatment, the different surface chemistries and morphologies of boiled and etched surfaces, the chemical differences between polished and boiled surfaces, and the similar chemistries yet differing morphologies of ET and PT surfaces will allow us to interpret 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 Fig. 1 will be beneficial in separating the effects of surface morphology from those of surface chemistry on the properties of single PEEK splats.

Splats deposited on substrates held at 323 °C during spraying were affected by surface pretreatment. Increasing substrate temperature will not have a significant effect on the surface chemistry of the substrates as the dehydration reactions driven by thermal energy take a significant length of time to reach equilibrium (Ref 20), and the splats were deposited on substrates immediately after the desired substrate temperature was reached. Characteristic images of the PEEK splats on polished, boiled, and etched substrates are shown in Fig. 3. As shown in Fig. 4, fewer splats were deposited on an E surface than were deposited on a B surface, which had fewer splats than a P surface. This trend was repeated with the thermally treated surfaces with ET having fewer splats than BT, which had fewer splats than a PT surface. However, there was no difference between the thermally treated and nonthermally treated samples, with B and BT, E and ET, and P and PT surfaces having similar numbers of splats. This relationship appears to be governed by surface roughness primarily, although it is likely to have a surface chemistry aspect as well. The lower splat area density due to surface roughness is likely due to a mechanism associated with reduced contact area resulting in reduced bonding area and therefore adherence of fewer splats. Results following a similar trend are exhibited for average splat area, but due to greater variability of these results, as displayed in Fig. 5, they must be considered statistically the same. The variability of splat area on each substrate was primarily determined by the variability of the PEEK particles that are impacting and adhering to the aluminum surfaces, which show an even distribution over the size range of 0-100 μm, as shown in Fig. 2. The smaller diameter of splats on E and ET surfaces (although not statistically significant) is likely due to increased fingering and fragmentation of particles, which is consistent with the lower circularity of splats on these substrates, as shown in Fig. 6.

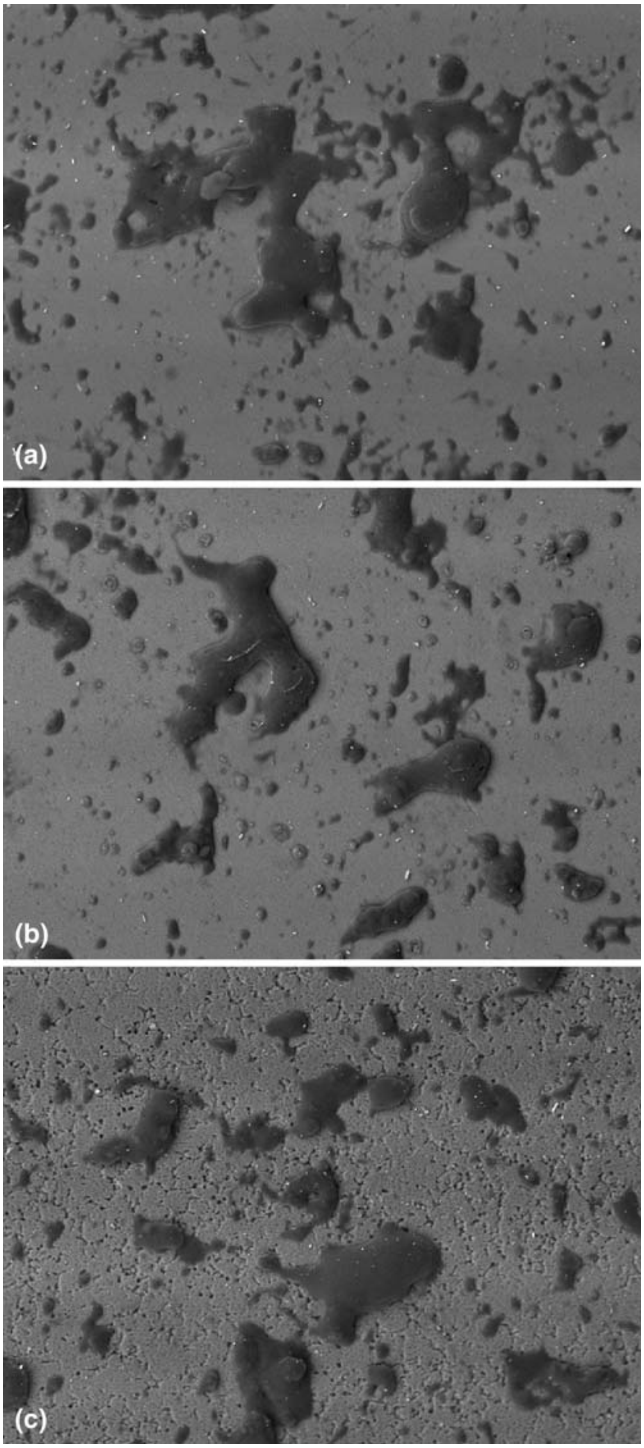

Fig. 3 Characteristic splat images on (a) polished, (b) boiled, and (c) etched substrates

The trend of surface morphology influencing splat morphology is continued to splat circularity, as displayed in Fig. 6. For substrates held at 323 °C, surface roughness appears to govern splat circularity, with E and ET surfaces

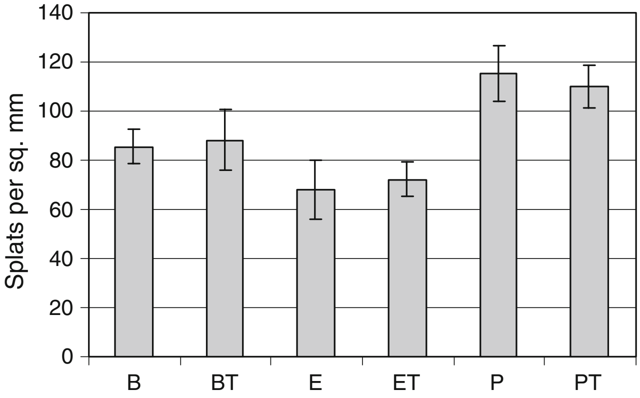

Fig. 4 Area density of splats deposited on each of the 6 pretreated substrates. Error bars represent the standard deviation associated to the average value

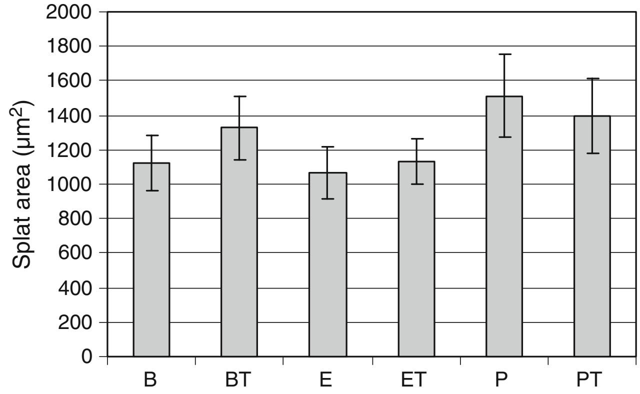

Fig. 5 Average area of individual splats deposited on each of the 6 pretreated substrates. Error bars represent the standard deviation associated to the average value

having splats with the lowest circularity, and B, BT, P, and PT surfaces having splats of similar circularity and similar surface roughness. This is an expected result as rougher surfaces will lead to more instability and variability of flow within the splats upon impact and, as such, result in a greater degree of fingering and less circular splats.

The majority of these results can be solely attributed to the different roughnesses of the 6 substrates, especially for the splat area and circularity results. Surface chemistry differences between the substrates can be discounted as ET and PT surfaces have essentially identical surface chemistries, yet the differences in splat morphology and surface roughness between these two pretreatments are marked.

Splat area density however appears to be affected by both surface chemistry and substrate morphology, and while substrate roughness definitely plays a contributing role to the splat area density, the difference in splat adhesion between B and P substrates and between BT and PT substrates cannot be solely ascribed to the small difference in roughness between these surfaces. It is thought that this difference in splat area density can be ascribed to

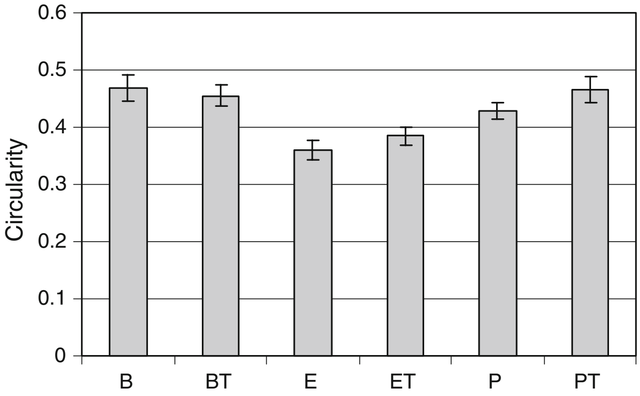

Fig. 6 Average circularity of the splats deposited on each of the 6 pretreated substrates. Error bars represent the standard deviation associated to the average value

the differing surface chemistries of the substrates in question. The boiled substrates, with an AlOOH surface layer, were significantly different from the 65% oxide, 35% hydroxide surfaces of P and PT substrates. It is thought that heating of the substrate by impacting PEEK particles releases water vapor due to desorption of chemisorbed water and dehydration of the AlOOH, by the reaction (Ref 20):

$$2\mathrm{AlOOH} \rightarrow \gamma\text{-}\mathrm{Al_2O_3} + \mathrm{H_2O}$$

The release of water vapor from B and BT substrates would therefore act as a vapor cushion between impacting PEEK particles and the substrate, resulting in particles of lower velocities not achieving sufficient contact area to adhere to the substrate. This low adhesion of PEEK to boiled surfaces has been seen in other, unpublished, areas of this study, and in the work of Trompetter, who found that NiCr particles exhibit poor deposition on boiled aluminum substrates (Ref 22).

4. Conclusions

Surface morphology was the main factor found to influence the splat area density, the area of single splats, and the circularity of single splats of HVAF-sprayed PEEK on substrates maintained at 323 °C. Substrate surface chemistry was however found to have an influence on the area density of deposited single splats, where surface morphology alone cannot explain the significant differences between the 6 different pretreated substrates.

References

1. Victrex plc, Food Processing Flyer, *Victrex Technical Information*, Victrex plc, 2006. http://www.victrex.com/adm/literature_files/Food_Processing.pdf
2. Victrex plc, Chemical Resistance Flyer, *Victrex Technical Information*, Victrex plc, 2006. http://www.victrex.com/adm/literature_files/Chemical_Resistance.pdf
3. Z.P. Lu and K. Friedrich, On Sliding Friction and Wear of PEEK and Its Composites, *Wear*, 1995, **181-183**(Part 2), p 624-631

4. L. Jacobs, M.M. Hyland, and M. De Bonte, Comparative Study of WC-Cermet Coatings Sprayed Via the HVOF and the HVAF Process, *J. Therm. Spray Technol.*, 1998, **7**, p 213-218
5. J.A. Browning, Hypervelocity Impact Fusion – A Technical Note, *J. Therm. Spray Technol.*, 1992, **1**, p 289-292
6. J. Cedelle, M. Vardelle, P. Fauchais, and Y. Tanaka, Effect of Substrate Surface Topography and Temperature, on Millimeter and Micrometer Sized Splat Formation and on Thermal Contact Resistance, *ITSC 2006: Pushing the Envelope of Materials Performance*, ASM International, 2006
7. P. Fauchais, M. Fukumoto, A. Vardelle, and M. Vardelle, Knowledge Concerning Splat Formation: An Invited Review, *J. Therm. Spray Technol.*, 2004, **13**(3), p 337-360
8. M. Fukumoto, H. Nagai, T. Yasui, Influence of Surface Character Change of Substrate Due to Heating on Flattening Behaviour of Thermal Sprayed Particle, *ITSC 2006: Building on 100 Years of Success*, B. Marple, Ed., ASM International, 2006
9. A. McDonald, M. Raessi, S. Chandra, J. Mostaghimi, and C. Moreau, Fragmentation of Plasma-Sprayed Molybdenum Particles on Glass Surfaces, *ITSC 2006: Building on 100 Years of Success*, B. Marple, Ed., ASM International, 2006
10. E. Petrovicova and L.S. Schadler, Thermal Spraying of Polymers, *Int. Mater. Rev.*, 2002, **47**(4), p 169-190
11. M. Ivosevic, R.A. Cairncross, and R. Knight, 3D Predictions of Thermally Sprayed Polymer Splats: Modelling Particle Acceleration, Heating and Deformation on Impact with a Flat Substrate, *Int. J. Heat Mass Transf.*, 2006, **49**, p 3285-3297
12. M. Fukumoto, E. Nishioka, and T. Nishiyama, New Criterion for Splashing in Flattening of Thermal Sprayed Particles onto Flat Substrate Surface, *Surf. Coat. Technol.*, 2002, **161**, p 103-110
13. S. Sampath and X. Jiang, Splat Formation and Microstructure Development During Plasma Spraying: Deposition Temperature Effects, *Mater. Sci. Eng. A*, 2001, **304-306**, p 144-150
14. J.R.T. Branco and S.V. Campos, Wear Behaviour of Thermally Sprayed PET, *Surf. Coat. Technol.*, 1999, **120-121**, p 476-481
15. R.S. Lima, A.S. Takimi, M.D. Lima, and C.P. Bergmann, Production of Recycled Polyethylene Terephthalate Coatings by HVOF and Plasma Spray, *Thermal Spray: A United Forum for Scientific and Technological Advances*, C.C. Berndt, Ed., ASM International, 1997
16. T.E. Twardowski, X.H. Fang, and R. Knight, Structure and Properties of Thermally Sprayed Amorphous Polymer Coatings, *ITSC 2000: 1st International Thermal Spray Conference*, May 8-11, 2000 (Montreal, Quebec), Canada, 2000
17. G. Zhang, H. Liao, M. Cherigui, and C. Coddet, Effect of Crystalline Structure on the Hardness and Interfacial Adhesion of Flame Sprayed PEEK Coatings, *ITSC 2006: Building on 100 Years of Success*, B. Marple, M. Hyland, Y. Lau, R.S. Lima, and J. Voyer, Eds., ASM International, 2006
18. W.S. Rasband, *ImageJ*, U.S. National Institutes of Health, 1997-2006
19. R.S. Alwitt, The Aluminium-Water System, *Oxides and Oxide Films*, J.W. Diggle and A.K. Vijh, Eds., Marcel Dekker, 1976, p 169-254
20. K. Wefers and C. Misra, *Oxides and Hydroxides of Aluminium*, Aluminium Company of America, 1987
21. E. McCafferty and J.P. Wightman, Determination of the Concentration of Surface Hydroxyl Groups on Metal Oxide Films by a Quantitative XPS Method, *Surf. Interface Anal.*, 1998, **26**, p 549-564
22. W.J. Trompetter, ''Splat-Substrate Interactions in High Velocity Thermal Spray Coatings: A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy in Engineering,'' Ph.D. Thesis, University of Auckland
23. S.X. Lu, P. Cebe, and M. Capel, Thermal Stability and Thermal Expansion Studies of PEEK and Related Polyimides, *Polymer*, 1996, **37**(14), p 2999-3009