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Study of the Splat-Substrate Interface for a PEEK Coating Plasma-Sprayed onto Aluminum Substrates

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The quality of coatings made using thermal spray processes depends greatly on the degree of adhesion between the substrate and its coating. Yet the bonding mechanisms between a substrate and coating are not well understood. In this study, polyetheretherketone (PEEK) powder was plasma-sprayed to form single splats on aluminum substrates, which had undergone various surface treatments, including boiled (BT), etched (E, ET), and polished (PT), all of which had also been thermally treated to remove water from the substrate surface, with the exception of one etched aluminum substrate. Scanning electron microscopy was used to give an overview of the surface and splat morphology. The splat-substrate interfaces were studied in detail using focused ion beam imaging and transmission electron microscopy, to characterize microstructural features within the splat-substrate interface, including inter/intrasplat pores, pores along the splat-substrate interface, level of contact between the splat and the substrate, etc. The results showed that the splat-substrate interface for the BT and the E substrate surface had poor level of contact, with a high number of small pores (<1 μm) along the splat-substrate interface for the BT splat-substrate interface, and the formation of a near-continuous crevice between the PEEK splat and the aluminum substrate for the E substrate surface. The presence of the fine needle-like network of oxide layer on the BT substrate surface may have restricted the flow of the molten PEEK on the aluminum substrate, and the possible presence of physisorbed and chemisorbed water on the E substrate surface may have reduced the level of contact between the PEEK and the aluminum substrate. In contrast, specimens which had undergone thermal treatment to minimize the presence of water on the substrate surface, such as the ET and PT substrate surface, exhibited high level of contact at the splat-substrate interface. The number of pores for the ET and the PT splat-substrate interfaces were substantially lower than of the BT and E splat-substrate interface.

Keywords image analysis, low power plasma spray, SEM, splat morphology, substrate treatment, surface preparation, TEM

1. Introduction

Many industries utilize components that are subjected to corrosion, high temperature, abrasion, etc., and such components rely on thermal spray processes for protection when operating under these environments. Thermal spray coatings provide a cost-effective way to protect and prolong the lifespan of components. For example, PEEK coatings have application in engine pistons due to their excellent thermal stability and tribological properties (Ref 1). The quality of thermal spray coatings made depends on various factors, including mechanical bonding, surface chemistry, spray conditions, porosity, etc. (Ref 2). A number of studies have been performed that have investigated the effect of surface condition on splat morphology. For example, Guilemany et al. found that with high velocity oxy-fuel sprayed (HVOF) WC-Co coatings on a Cu substrate, the interface structure depended significantly on the morphology of the substrate surface (Ref 3). Similarly, Mellali et al. showed that while increasing substrate roughness by grit blasting may improve ceramic coating adhesion, there is a roughness value threshold beyond which the level of adhesion will decrease, along with the potential negative effect of grit residue which may also decrease coating adhesion (Ref 4). The importance of surface chemistry on splat formation was demonstrated by Withy et al., who showed that the presence of aluminum oxyhydroxide (AlOOH) on the aluminum substrate surface caused the area density of PEEK splats to be significantly lowered compared to a

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polished Al substrate surface, which had mainly oxide and hydroxide on its surface. It was suggested that the heating of the substrate surface by the impacting PEEK particles led to the removal of chemisorbed water and the dehydration of the AlOOH. The release of water vapor may have also created a vapor cushion which hindered the PEEK particles from adhering to the Al substrate surface (Ref 5). Other works have shown that the presence of organic surface films can inhibit splat adhesion (Ref 6).

Aluminum is a very ductile metal with a relatively low (~600 °C) melting point. During the thermal spray process, the aluminum substrate might be subjected to high temperature and high stress from impacts made by molten spray material. This may alter its surface chemistry and microstructure and, in turn, can affect the degree of adhesion between the splat and the substrate. Polyetheretherketone (PEEK) is a tough, semicrystalline thermoplastic with a glass transition temperature of ~143 °C and a melting temperature of 334 °C (Ref 7). It has excellent thermal, mechanical, and tribological properties that make it an ideal candidate material for coatings.

As part of a larger study of the effects of thermal spray methods, substrate surface treatments and temperature, on splat morphology, splat-substrate interfacial microstructure and the level of adhesion at the splat-substrate interface, microstructural features such as pores and the different phases existing at the splat-substrate interface were studied for the plasma-sprayed PEEK powder onto aluminum substrates. These substrates will undergo several different surface treatments to produce different surface chemistry and roughness. This paper will mainly focus on the microstructural characterization of the splat-substrate interfaces from these different aluminum substrates, to determine the effects of surface condition on the level of adhesion between the splats and the substrate.

2. Experimental Procedures

Low power spraying conditions were used for PEEK, which has a low melting and degradation temperature (Ref 8). ICI Victrex PEEK polymer fine powder was used as the spray material. It has a size distribution of 10-200 μm, with an average size of ~50 μm. Single splats were sprayed by using a Sulzer Metco 7 MB plasma system operating at 150 A with 40 standard liters per minute (SLPM) of N_2 at spray distances of 80 mm. 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 powder feeder used was a Praxair 1264 rotating slot powder feeder (Praxair Surface Technologies, IN). Powder was fed at rates of approximately 10-20 g/min, at an angle of 30° anticlockwise from the line of jet direction. The torch was mounted on an industrial robot, with splats deposited in a single pass at a 0.5 m s^{-1}.The substrate surfaces were held at room temperature (~23 °C).

Four different surface treatments were chosen. The boiled substrate was placed into boiling water for 30 min. The aim was to change the surface chemistry by growing surface oxide and hydroxide. Etched substrates were chemically treated by a solution consisting of a mixture of H_2SO_4 and HF, and the polished substrate was ground and mirror polished mechanically using a diamond paste with a grit size of 1 μm. Finally, the three substrates (designated BT, ET, and PT) were thermally treated by heating at 350 °C for 90 min in air in order to remove the physisorbed and chemisorbed water on the substrate surfaces. According to Tran et al., thermal treatment at 350 °C of boiled aluminum substrates released water vapor from the substrate surface and led to dehydration of the oxyhydroxide (Ref 9). For comparison, studies were also performed on the etched surface, without thermal treatment (designated E).

Samples for scanning electron microscopy (SEM) were gold-coated prior to examination in a Hitachi S-3400 SEM to examine the surface morphology of the specimen. The type of surface features which were examined included surface roughness, splat thickness, and splat size. Focused ion beam (FIB) milling, with the use of FEI XP200, generated cross-sectional images revealing the interfacial structures between splats and the substrate surface. Protective platinum straps were deposited in situ in the FIB on to the surface prior to milling. A large number of FIB cross sections were made for PEEK splats on all substrates for various splat sizes and thicknesses. This ensured that the images presented were representative of the splat-substrates under examination. The FIB was also used to prepare transmission electron microscopy (TEM) samples. Once TEM samples were made, they were lifted out using a nano-manipulator and put on to a C-coated Cu grid. TEM samples will be examined using Philips CM 200 to provide high-resolution images of the splat-substrate interfacial features.

Statistical analyses were performed on low magnification SEM images to determine the average splat diameter for each substrate type. Splats within an area of 1 mm by 1 mm were measured to calculate the average splat diameter and the degree of circularity of splats. The average splat diameters for each of the substrate surface types were found to be of similar values; all were ~60 ± 5 μm. The degree of circularity for splats on the BT substrate surface was slightly lower than of the ET and PT substrate surfaces.

3. Experimental Results

Several different surface treatment methods were used to vary the substrate surface, which resulted in various degrees of surface roughness. The SEM images presented here give an approximation for surface roughness. Polished samples having relatively flat substrate surface with surface roughness within a few tens of nanometers. The substrate surface of the etched samples was heavily pitted, with a surface roughness of around 1 μm.

In Fig. 1, the high magnification SEM images were taken from plasma-sprayed single splats on the BT, ET, and PT substrate surfaces. The BT substrate surface exhibited a slightly roughened and textured surface. The ET substrate surface exhibited a large number of pores and with a roughened surface, while the PT substrate surface had no visible pores and it appeared to be relatively flat. The single splats appeared to be substantially unmelted on all three substrate surfaces, with localized melting of the splats around their periphery indicated, for example, by the regions marked X in Fig. 1(a).

Figure 2 is a secondary electron FIB image showing a cross section prepared through the locally melted region at the periphery of a PEEK splat sprayed on to the BT substrate at 23 °C. Inset is a plan view image showing the location of the milled cross section relative to the splat location. In this region, the PEEK splat is relatively thin (~2 μm) even though the splat diameter was ~50 μm with a low degree of circularity. The cross-sectional image shows polycrystalline grain structure of the aluminum substrate, together with a layer of externally grown oxide ~500 nm in thickness. The oxide is nonuniform in thickness and on the left of the image it can be seen to have grown locally into the aluminum substrate. The PEEK splat is attached to the oxide layer, with some degree of delamination near the center. It is non-uniform in cross section ranging from a few 10s of nanometers in thickness to several microns. At the splat-substrate interface between the PEEK splat and the oxide layer, there are many pores of a few 10s of nanometers in size.

Figure 3 is a secondary electron FIB image showing a cross section prepared through an unmelted region at the periphery of a PEEK splat sprayed onto the BT substrate at 23 °C. The inset is a plan view image indicating the location of the cross section. In this region, the PEEK splat is relatively thick (>20 μm). Similar to Fig. 2, the externally grown aluminum oxide layer is evident, the PEEK splat was again seen to be attached to the oxide layer, but it is nonuniform in thickness and at the splat-substrate interface between the PEEK splat and the oxide

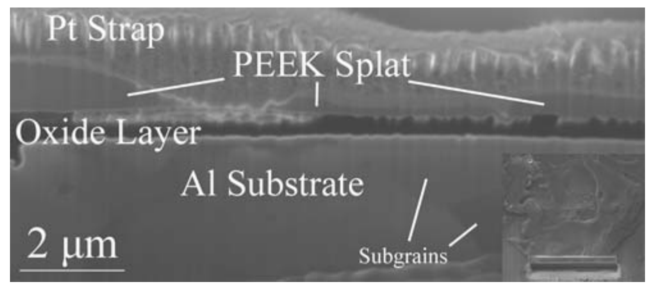

Fig. 2 FIB cross section of a plasma-sprayed melted splat on the BT substrate surface held at 23 °C (Inset shows plan view image indicating location of cross section)

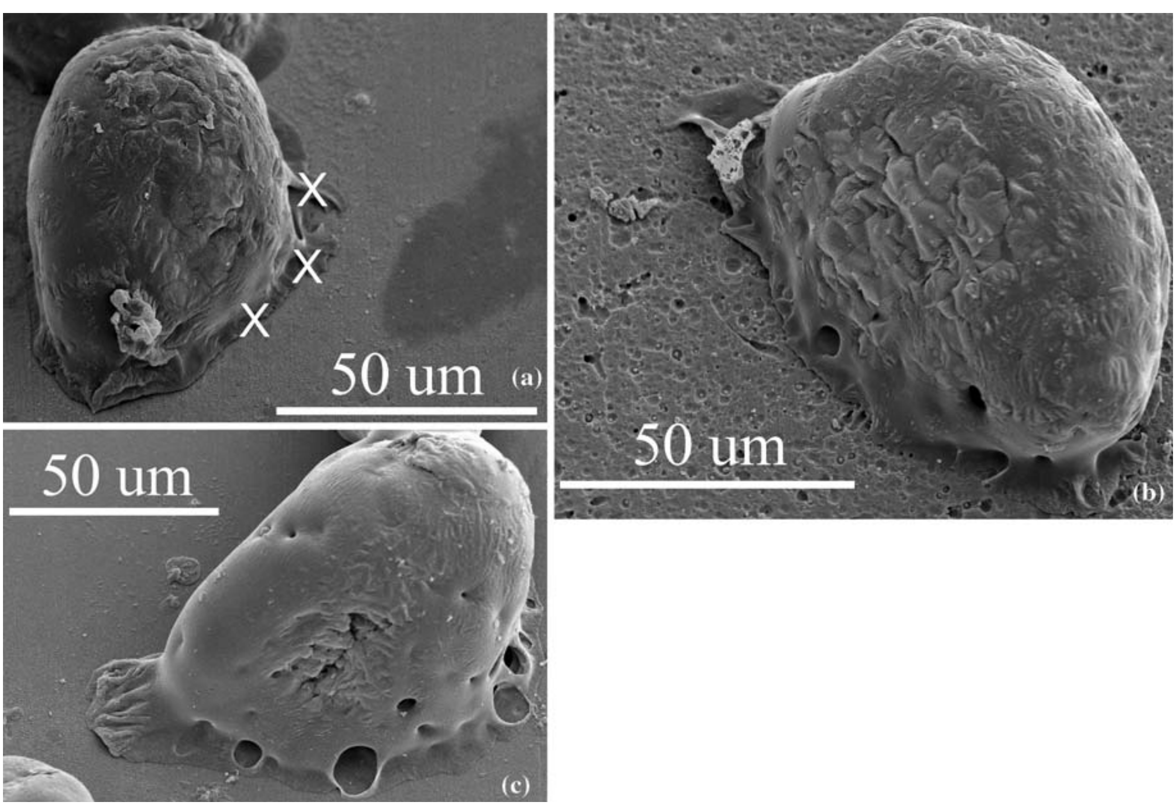

Fig. 1 SEM images of plasma-sprayed splats from the BT (a), ET (b), and PT (c) substrate surface held at 23 °C

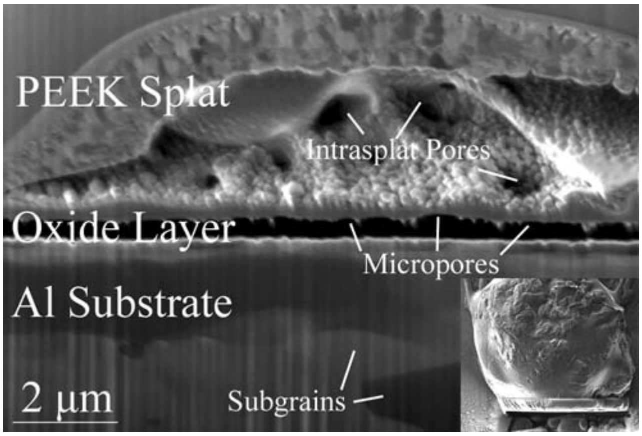

Fig. 3 FIB cross section of a plasma-sprayed thick splat on the BT substrate surface held at 23 °C (Inset shows plan view image indicating location of cross section)

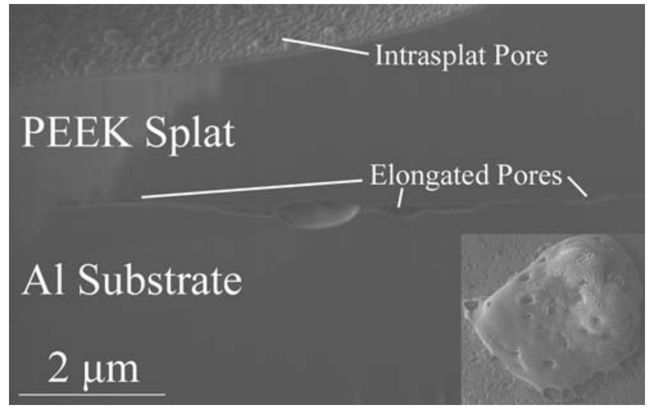

Fig. 5 FIB cross section of a plasma-sprayed thick splat on the E substrate surface held at 23 °C (Inset shows plan view image indicating location of cross section)

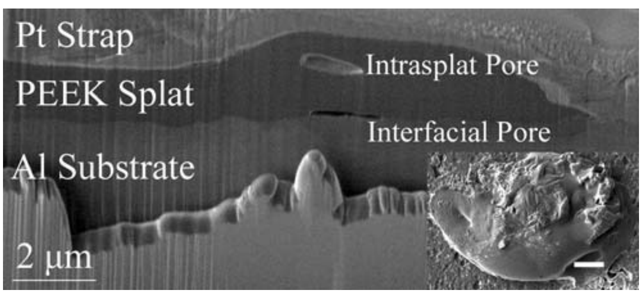

Fig. 4 FIB cross section of a plasma-sprayed thin splat on the ET substrate surface held at 23 °C (Inset shows plan view image indicating location of cross section)

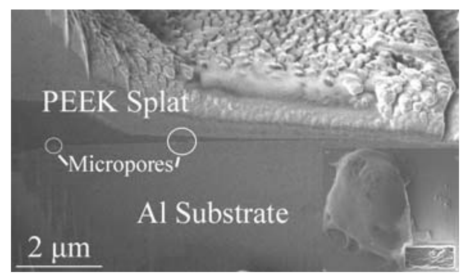

Fig. 6 FIB cross section of a plasma-sprayed thick splat on the PT substrate surface held at 23 °C (Inset shows plan view image indicating location of cross section)

layer, there are again many pores in the size of a few 10s of nanometers present. According to Withy et al., XPS analysis has shown that this layer is composed of varying amounts of Al_2O_3, $Al(OH)_3$, AlOOH, and chemisorbed water. As noted above the layer generated through pretreatment is around 500 nm thick (Ref 10). The PEEK splat also contains a very large intrasplat pore several microns in diameter. Since the PEEK particles were fully melted during spraying, it is assumed that any pores present within the resultant PEEK splats were formed during solidification.

Figure 4 is a secondary electron FIB image showing a cross section prepared through the locally melted region at the periphery of a PEEK splat sprayed onto the ET substrate at 23 °C. The location of the cross section is indicated by the white, horizontal line on the inset plan view image. The PEEK splat in this region is relatively thin (~2-3 μm). There is, however, a high degree of contact between the PEEK splat and the substrate with an elongated pore ~2 μm in length found along this interface. This high degree of contact is apparent even though the substrate surface is relatively nonuniform and appears to undulate. There is also an elliptical pore of ~2 μm in length found within the PEEK splat itself.

Figure 5 is a secondary electron FIB image showing a cross section prepared through an unmelted region of a PEEK splat on the E substrate at 23 °C. The location of the cross section is indicated by the black, horizontal line on the inset plan view image. A large intrasplat pore, 10s of micrometers in diameter, is partially visible at the top of the image. Along the splat-substrate interface, there is a series of elongated pores, each <2 μm in length, forming a near-continuous crevice between the splat and the substrate. This shows that the level of adhesion across the interface is very poor, especially in comparison to the cross section shown in Fig. 4 from the ET-treated surface.

Figure 6 is a secondary electron FIB image showing a cross section prepared through the locally melted region at the periphery of a PEEK splat sprayed, through to the unmelted region on the PT substrate. The thickness of the PEEK splat varies from <1 μm at the periphery, to >4 μm at the unmelted region, with the gradual increase in thickness from the melted periphery to the unmelted region. The PT substrate surface is relatively flat compared to the BT and the ET substrates. There is a high degree of contact between the PEEK splat and the substrate from the locally melted PEEK splat through to the unmelted PEEK splat region. However, there are several

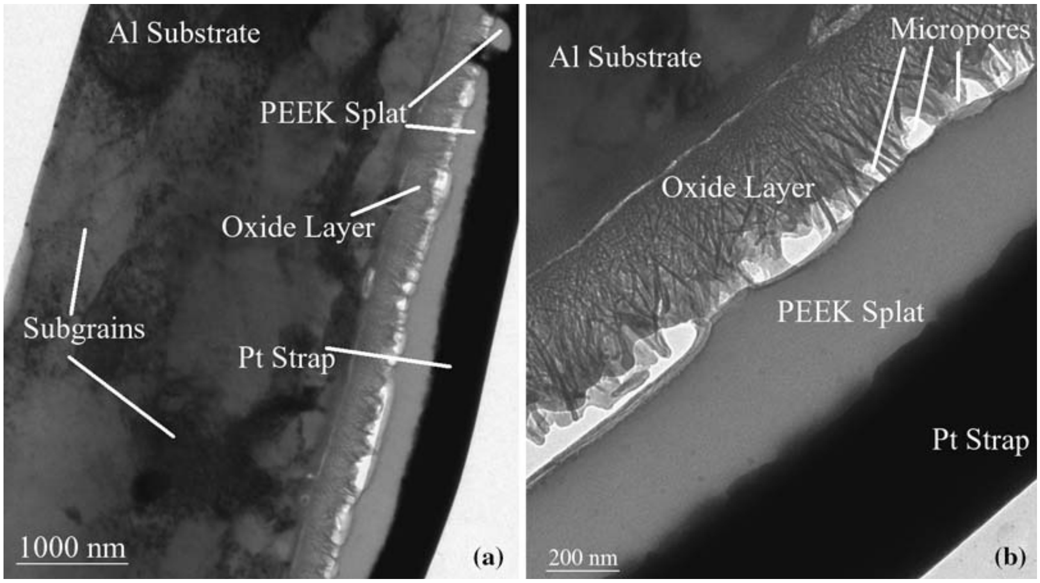

Fig. 7 Low (a) and high (b) magnification bright field TEM images made from the plasma-sprayed PEEK splat on the BT substrate surface held at 23 °C

very fine pores, <100 nm in diameter (circled), found along the splat-substrate interface.

Figure 7(a) shows a low magnification bright field TEM image of the plasma-sprayed PEEK splat on the BT substrate held at 23 °C. This section was prepared through a region where the splat was locally melted, similar to the splat shown in Fig. 2. The black portion on the right hand side shows the protective Pt strap deposited using the FIB during specimen preparation. To the left of this is the PEEK splat, followed by the oxide layer, and then the aluminum substrate. This TEM image is consistent with the FIB cross-sectional image shown in Fig. 2, showing poor contact between the oxide layer and the PEEK splat and the micropores (<50 nm) found along the splat-substrate interface. This TEM image also shows more clearly the deformation of the aluminum substrate, where a high dislocation density and a number of poorly defined subgrains are present. Figure 7(b) shows a higher magnification bright field TEM image taken from the same sample. Upon closer inspection, the oxide layer consists of a network of needle-like structures formed on top of the aluminum substrate. It is evident that the needles have nucleated on the aluminum substrate and grown normal to that interface. Moreover, these needles appear to coarsen away from the substrate. It is also apparent that there is a layer ~50 nm thick has grown into the aluminum substrate. The identity of this phase is not clear. The PEEK splat layer appears to be in contact with the needle-network structure of the oxide layer at local regions, where the needles protruding outward to make contact with the PEEK splat. In general, the contact appears to be poor. It is possible that the delamination between the PEEK and the alumina is promoted by the preparation of thin electron transparent sections in the FIB, but it should be noted that the delamination between these phases is still not complete, which, when considered supports the notion that the contact between these phases is generally poor (Ref 11). Electron diffraction studies of the PEEK splat indicated that it was entirely amorphous, which suggests that no crystallization of this phase occurred upon solidification.

4. Discussion

The three surface treatments prepared yielded an aluminum substrate various level of surface roughness. There was an oxide surface on the BT substrate, a highly pitted and rough surface on the ET (and E) substrate, and the relatively flat PT substrate surface. These different surface treatments however, seemed to have little effect on the degree of flow of the molten PEEK splats as shown by the SEM images. Electron diffraction studies of the PEEK splat have indicated that the PEEK splat is entirely amorphous which suggests rapid cooling of the PEEK splat has occurred. One possible cause is that the substrate surfaces were all held at room temperature, which did not promote melting of the PEEK, but would promote rapid cooling of the splat. This is supported by studies by Mehdizadeh et al. who reported that an increase in substrate temperature could delay the solidification of molten particles (Ref 12).

The secondary electron FIB images for the cross section of the plasma-sprayed BT substrate in Fig. 2 and 3 showed that there was a low degree of adhesion between the PEEK splats and the substrate surface, with high number of nanoscale pores found along the splat-substrate interface. The TEM analysis was consistent with these observations. Both Siegmann and Brown (Ref 13) and Wang et al. (Ref 14) suggested that higher interfacial roughness would enhance the mechanical interlocking between the coating and the substrate. On the contrary, Palathai et al. had reported that the level of adhesion for

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PEEK coatings on aluminum substrate increased up to an interfacial roughness value of ~7 μm, but beyond this value there was no further increase of level of adhesion (Ref 15). One possible cause was claimed by Mehdizadeh et al. that excessive surface roughness may restrict the flow of the molten PEEK on the aluminum substrate (Ref 12). In this case, the BT substrate has a much lower level of roughness, but the low level of contact at the interface is poor, this suggests the oxide needle structure played an important role in the reduction in the wetting of the substrate leading to a low level of contact and the inhibition of the flow of the molten PEEK on the substrate. Another possible cause for the poor interfacial bond between the PEEK splat and the substrate surface is that the fine porosity formed on the substrate surface may trap moisture, which would be evaporated due to the sudden elevation of surface temperature when molten PEEK impacts upon the substrate surface.

In contrast, examination of the ET and PT splats show a high degree of adhesion between the splats and the substrates. The ET splat-substrate interface had an isolated pore at the interface, and the PT splat-substrate interface exhibited a few nanoscale pores. According to Zhang et al., the volume contraction of semi-crystalline PEEK coating during cooling results in tensile residual stresses sufficient in exceeding the bonding strength between the PEEK coating and the substrate (Ref 16). It is likely that these stresses give rise to the isolated pores seen at the splat-substrate interfaces for these surfaces. Given that the PEEK splats are amorphous, the relatively few pores present suggest that the volume contraction is smaller compared to semi-crystalline PEEK splats. The elongated pore found at the ET splat-substrate interface might be the result of a series of smaller pores in close proximity which have coalesced to form one continuous, elongated pore.

The comparison between the cross sections for the etched and etched and thermally treated surfaces indicate that the thermal treatment given to the aluminum substrate, which removes the chemisorbed water from the substrate surface significantly affects the level of adhesion between the PEEK splat and the aluminum substrate. This is consistent with Thorne et al. who showed that the formation of strongly bound aluminum trihydrate ($Al(OH)_3$) due to the presence of physisorbed and chemisorbed water on aluminum foil reduces the level of adhesion between polyethylene and the aluminum foil (Ref 17). This suggests that the thermal treatment given to the etched substrate surface prior the thermal spraying of PEEK powder, was beneficial by increasing the level of contact between the PEEK splat and the substrate, giving a higher quality coating of PEEK.

5. Conclusion

In this study, low power plasma spray process was used for the deposition of PEEK powder onto aluminum substrates treated to vary surface roughness or chemistry. The splat morphology for all substrate surfaces was very similar in terms of average splat shape and size. Most single PEEK splats on all substrate surfaces had localized melting at their periphery, but the majority of the splat itself remained unmelted. The splat-substrate interfacial structures varied between different substrate surface types. Of the four different substrate surfaces, both the etched (E) and the boiled and thermally (BT) treated substrate surfaces were shown to have poor level of contact between the splats and the substrate. For the BT substrate surface, there was high number of fine nanoscale pores at the splat-substrate interface. For the E substrate surface elongated pores found along the splat-substrate interface formed a near-continuous layer of poor adhesion. In contrast, the splat-substrate interface for both the etched and thermally treated and polished and thermally treated substrates exhibited a high degree of contact between the PEEK splat and the substrate. These suggest the surface chemistry of the aluminum substrate had greater influence over the level of contact than surface roughness.

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