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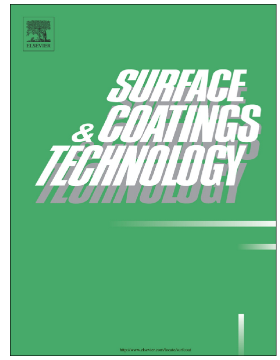

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Sudarshan Devaraj, Bobby Anand, Michael Gibbons, André McDonald, Sanjeev Chandra

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Thermal Spray Deposition of Aluminum and Zinc Coatings on Thermoplastics

Sudarshan Devaraj[1], Bobby Anand[1], Michael Gibbons[1], André McDonald [2], Sanjeev Chandra[1]

[1]*Department of Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario, M5S 3G8, Canada*

[2]*Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, T6G 1H9, Canada*

ABSTRACT

Coatings of aluminum and zinc were applied on two thermoplastic materials, ultra-high molecular weight polyethylene (PE) and polytetrafluoroethylene (PTFE), using twin wire-arc spray spraying. Samples were either smooth (R_a = 0.2 μm) or roughened by grit blasting (R_a = 1.6 μm). Before the start of spraying samples were kept at either room temperature or preheated to 55°C for PE and 95°C for PTFE, so that the peak temperature during spraying reached the glass transition temperature of the polymer. Surface temperature was monitored during spraying using thermocouples. Coating adhesion strength was measured using pull tests. Single splats of metal on samples were examined using SEM images. Zinc coatings, about 260 ± 20 μm thick, formed on both polymer samples irrespective of their surface roughness. Adhesion strength was significantly higher on rough surfaces than smooth surfaces. Increasing the initial sample temperature also enhanced adhesion strength. Aluminum adhered only to the PTFE but not the PE. Aluminum droplets have a higher melting point than zinc and melted the sample upon impact, inhibiting mechanical bonding. These results suggest that the metal adhesion to thermoplastics can be significantly improved by pre-heating polymer samples prior to thermal spraying.

KEYWORDS

Polymer metallization, metal coating adhesion, polymer-metal composites, thermoplastics, wire-arc spraying, droplet impact.

1. INTRODUCTION

Polymeric materials are employed in many industrial applications as they are light, relatively cheap, and can be easily processed; however, they are also soft and have low thermal and electrical conductivity, which limits their usefulness. The surface properties of polymers can be modified by applying coatings on them, creating lightweight composite materials that can be very useful in specific applications **[1, 2, 3]. Chen *et al.* [3] characterized the thermal performance of zinc sprayed Acrylonitrile Butadiene Styrene (ABS) substrates as heatsinks for Light Emitting Diode (LED) cooling applications and found that these composite materials could provide significant weight reduction in the heatsinks.** Thermal spray coating is a widely used method of applying metal coatings by directing a molten metal spray onto a solid surface. One technology, wire-arc spraying, is a low-cost and well-developed way of applying metallic coatings. In this process an electric arc is struck between the tips of two continuously fed wires and a compressed air jet is used to strip off molten metal droplets and direct them onto a substrate where they coalesce and freeze to form a solid layer [3]. Though this is a well-known coating method little research has been done on the metallization of polymers using wire-arc systems.

Gonzalez *et al.* [4] summarized the current state of the art for thermal spray metallization of polymers and found that the low melting point and soft nature of most thermoplastics made it difficult to apply metal coatings on them using high-temperature thermal spray techniques. Thermoplastics, in particular, have comparatively low melting points [5] and can be severely damaged when molten metal particles and hot gases impinge on them. Thermosetting plastics have higher heat-resistance than thermoplastics, which reduces structural damage even at the elevated temperatures they experience when subjected to a thermal spray.

Cold spraying, which has inherently low operating temperatures, has also been examined as a method of coating thermoplastics [7,8]. Vucko *et al.* [7] embedded Cu particles into high-density polyethylene (HDPE) (a thermoplastic) for anti-fouling applications using cold spraying but did not report deposition of contiguous copper coatings in their work. Ganesan *et al.* [8] investigated the deposition efficiency of spherical and dendritic copper powder on both polyvinyl chloride (PVC) (a thermoplastic) and brittle epoxy (a thermoset) substrates using the cold spray technique. They showed that the particles could adhere to the PVC substrate due to its highly plastic nature and substrate damage was less than that inflicted on epoxy substrates. Che *et al*. [9] cold sprayed Cu particles onto CFRP (Carbon Fiber Reinforced Polymer) (thermosetting matrix). They observed substrate erosion due to the large impact force of impinging metal particles when combined with the brittleness of the substrate. **However, good mechanical interlocking of Cu particles was achieved on the thermoplastic polymers (Polyether Ether Ketone (PEEK), Polyethylenimine (PEI) and ABS) used in their study. This was a result of thermal softening exhibited by the thermoplastics at temperatures close to their T_g, which promoted adhesion. Similarly, Rokni *et al.* [10] deposited dense Al coatings on PEEK, ABS and PEI using a high-pressure cold spray process.**

Some high-temperature thermal spray methods such as powder flame spray, electric wire-arc spray, plasma spray have been used successfully to coat thermosetting plastics like polyurethane (PU) and carbon fibre reinforced epoxy composites where the epoxy matrix was a thermoset [[11], [12], [14]]. Ashrafizadeh *et al.* [11] co-cured PU with Al-12Si particles on the surface before flame spraying with Al-12Si. This approach minimized direct contact of impacting particles with PU substrates, avoiding localized melting and decomposition of the low melting temperature polymer. **However, Liu *et al.* [15] deposited Zn and Al bond coat layer (~50 µm),**

using both plasma and electric wire-arc spraying process, on Graphite fiber-reinforced polyimide (thermoset) without any interlayer. Therefore, when using high-temperature thermal spray techniques to deposit a metal coating, the need for an interlayer depends on the heat sensitive nature of the polymers and the applications targeted. Polymer matrix composites which have high temperature resistant reinforcements are generally sprayed without the use of an interlayer [15, 16, 17]. Polymers with very low melting temperatures require an interlayer to be first applied on the polymer substrate to protect it from damage by high-temperature gases and molten particles impinging on it [11,18].

The effect of varying substrate temperature on adhesion of thermal spray coatings is well established [19]. Pershin *et al.* [20] showed that coating adhesion strength of nickel coatings on steel could be significantly improved by heating the substrate before coating. Che *et al.* [21] studied cold spraying on thermoplastics and investigated the effect of varying carrier gas temperature during on particle penetration. They observed that particles propelled by gas whose temperature was higher than the glass transition temperature (T_g) of the polymer substrate penetrated deeper into it than those in gas at a temperature below T_g**. This resulted in development of thick metallic coatings of tin and copper onto these thermoplastics. Similarly, Ganesan *et al.* [8] showed that the deposition efficiency of Cu particles, deposited on PVC substrates by cold spraying method, increased with increase in the gas temperature of the process up to the T_g value of PVC. The thermal softening behaviour exhibited by these thermoplastics close to or higher than their T_g aids metal particle penetration into the softened polymer substrates. This eventually leads to strong mechanical interlocking of the metallic particles with the substrates upon cooling. Therefore, by controlling the gas temperature in the cold spray process, thick metallic coatings could be achieved on**

thermoplastic substrates. The results from cold spraying metals on polymers highlight the importance of polymer substrate temperature during spraying. However, in all previous studies only the carrier gas temperature was measured, not the actual substrate temperature during spraying, which would be important to know since significant changes in polymer properties can occur within a small temperature range [22,23].

Sandblasting metallic substrates prior to thermal spraying to increase their roughness is the most common way of achieving strong mechanical interlocking of coating particles with the substrate. However, the process of sandblasting polymer substrates can produce significant damage as demonstrated by Ganesan *et al.* [13] who concluded that sandblasting thermoset CFRP structures caused localized destruction of the polymer surface**. Sandblasting polymer matrix composites which have brittle fiber reinforcements is not a viable option. Therefore, other surface preparation methods like co-curing of metallic mesh and powder into the CFRP substrates have been used to enhance the bond strength of the coatings [24].** Thermoplastics, by contrast, have excellent impact resistance, which makes them suitable for mechanical roughening processes. **The difficulty in achieving a uniform surface roughness on the polymers by grit blasting has limited research in this direction [13].**

In this study aluminum and zinc coatings were applied onto two different thermoplastic polymers, ultra-high molecular weight polyethylene (PE) and polytetrafluoroethylene (PTFE), using wire-arc spraying. Surface roughness was varied by grit blasting and substrate temperature was varied during spraying by placing it on a heater block. Substrate temperature variation during spraying was monitored by thermocouples. Coating cross-sections were examined using SEM images and coating adhesion strength measured by conducting pull tests. Single splats formed by impact and solidification of metal droplets were also collected on the different substrates and examined under a microscope to understand why adhesion strength varied with surface roughness and temperature.

2. EXPERIMENTAL METHOD

2.1 Wire-Arc Spraying

A high-density wire-arc spray coating system (Thermion, Silverdale, Washington, USA, P/N: 57456) was used to coat the polymer substrates. Commercially available pure Al (Oerlikon Metco, Westbury NY, USA, DSMTS-0003.10) and Zn (Oerlikon Metco, Westbury NY, USA, DSMTS-0010.6) wires were used in this study. Some important thermophysical properties of the coating metals are listed in Table 1. The mean size of the Al and Zn spray particles was determined by spraying the metal particles into a water bath and then allowing them to dry under natural convection. Particle size distribution of both Al and Zn particles was obtained using a Malvern Mastersizer X laser analyser (Malvern Instruments Ltd., Malvern, Worcestershire, UK, P/N: 2000).

All spray parameters for Al and Zn were kept constant except the input arc voltage, which was 32 V for Al and 28 V for Zn. Dry air was chosen as the atomizing gas and the gas pressure was fixed at 690 kPa (100 psig). A nozzle stand-off distance of 152 mm (6 in) was used. All samples used in this work were cooled using compressed air during spraying. **The pressure of the cooling air was 690 kPa (100 psig).** The robotic arm holding the spray nozzle was programmed to move at a speed of 1000 mm/min in a serpentine pattern consisting of parallel passes spaced 5 mm apart. Identical process parameters (e.g., gas pressure, stand-off distance) were used for single splat studies.

2.2 Experimental Assembly for Single Splat and Coating Deposition

The experimental facility used for depositing a thick metallic coating on the polymers is shown in Figure 1. This assembly was used for spraying samples at both room temperature and elevated temperatures. **Some of the polymer samples were heated prior to thermal spraying to investigate the effect of polymer substrate temperature on coating bond strength.** The samples to be heated were clamped to a heating block whose temperature was monitored with a Proportional-Integral-Derivative (PID) controller (Omega, Laval, Canada, P/N: C9000A). This block was machined to hold three cartridge heaters (OMEGALUX™ CS, Omega, Laval, Canada, 350 W, P/N: CSS-10150) to heat the system to the desired temperature. Power to the heaters was controlled by a variable voltage power supply. The polymer samples were heated using a 320 W electrical resistance heater (KHA-808/5, Omega, St-Eustachse, Quebec, Canada,) while measuring and controlling the sample surface temperature using K-type thermocouples and a PID controller, respectively. **Heating experiments were only carried out on smooth polymer samples and rough polymers were not considered for this study. The PTFE samples were heated at a rate of 5 °C/min and maintained at an elevated temperature of about 95 °C for 5 minutes before aluminum was sprayed on it. When spraying zinc on PE the substrates were preheated to 55°C (20 °C lower than the maximum operating temperature) before spraying.** The surface temperature of the polymer samples was recorded using five type-K thermocouples (FF-K-20-100, Omega), which were connected to a data acquisition module (DAQ-2408, Omega). The thermocouples were attached to the substrates through holes drilled through the heater block, and the thermocouple junctions were placed flush in contact with the substrate surface.

To capture single splats of metal on polymer surfaces a protective metal barrier with a 1 mm diameter hole in it was placed between the spray and the substrate. After a single pass of the spray torch over the orifice individual metal splats that had passed through the hole could be observed on the polymer surface.

2.3 Polymeric Substrate Surfaces

Two thermoplastic substrate materials, Polytetrafluoroethylene (PTFE , McMaster-Carr, Sante Fe Springs, California, USA, P/N: 8545K24) and Ultra-high-molecular-weight polyethylene (PE, McMaster-Carr, Sante Fe Springs, California, USA, P/N: 8752K111), were used in this study. Table 2 lists their thermophysical properties. Polymer sheets as received from the manufacturer are labelled smooth in the entire study.

All substrate samples were cut into 50 mm x 50 mm pieces with a thickness of 3 mm. Samples were cleaned using isopropyl alcohol (99%, Commercial Alcohols, Brampton, ON, Canada, P/N: 028668) that was spread over the entire surface and allowed to dry to removes any contaminants [18].

The polymer sheets obtained from the manufacturer had roughness (R_a) values of approximately 0.20 ± 0.05 µm, which are called "smooth" in this paper**. In order to study the effect of polymer surface roughness on the adhesion strength of the coatings, the polymer surfaces were roughened by grit blasting with #20 aluminum oxide (3418K46, McMaster-Carr, Grand Haven, Michigan, USA) using a constant air pressure of 690 kPa (100 psig) and a nozzle-substrate stand-off distance of approximately 100 mm (4 in).** The surface roughness of all the samples was measured before deposition using a skid-reference profilometer (Precision Devices Inc., Michigan, USA, P/N: PDA-400ao) with at least 10 measurements taken for each sample. The average surface roughness (R_a) value after grit blasting was 1.60 ± 0.05 μm and these are labelled "rough" substrates.

2.4 Coating Cross-section Characterization

Coated polymer samples were mounted in epoxy resin, cut and polished. These samples were examined using a scanning electron microscope (SEM) (Hitachi Tabletop, country, P/N: TM 3000) at low voltage mode (5 V) to avoid specimen charging of the non-conducting polymer samples. To observe the cross-section of single metal particles deposited on polymers the samples were cooled with liquid nitrogen so that they became brittle and were easily broken by instigating a crack in the sample [28]. A focused ion beam (FIB) was used (NB 5000 Dual Beam) to take sections through particles embedded in the polymer. Parameters such as splat equivalent diameter, perimeter, circularity and degree of splashing were calculated using image processing software, ImageJ-NIH.

2.5 Adhesion Strength

Coating adhesion strength was measured using a pull test (PosiTest™ AT-M Manual Tester, DeFelsko, St. Catherines, Ontario, Canada, P/N: ATM20) as per ASTM standard D4541**. A total of 5 measurements were taken for each sample and error bars used to show the standard deviation in measurements.** A standard ATM20 Al pull stub with 20 mm diameter was bonded to the centre of the coated samples using an epoxy adhesive (Devcon No.19770 'plastic steel' two-part epoxy, Aurora, Ohio, USA, P/N: 19770). Once the epoxy hardened, the coating was pulled off using a stress range of 0.5 - 20 MPa.

3 RESULTS AND DISCUSSIONS

3.1 Particle Size Distribution of Aluminum and Zinc

Figure 2 shows SEM images of aluminum and zinc spray particles that were captured by spraying into a water bath. Most of the particles were irregular in shape and using a particle size analyzer the mean particle diameters (d_{50}) of aluminum and zinc were measured to be 78.6 um and 61.3 um, respectively, which are typical for wire-arc spraying [29,30,31]. Zinc has a higher density and lower surface tension than aluminum (see Table 1) and would be expected to fragment into smaller particles.

3.2 Substrate Surface Temperature

3.2.1 Samples at Room Temperature

Substrate temperature variation was recorded while the wire-arc spray torch made 10 alternating passes over the substrate. Figure 3 shows the measured temperature variation of rough PTFE surfaces while depositing either aluminum (Figure 3a) or zinc (Figure 3b) on them; the temperature variations on PE surfaces were very similar and are not shown.

The substrates were initially at room temperature (~25°C), which is also marked in the Figures. The 10 peaks observed in each Figure correspond to the passage of the spray torch over the substrate, followed by cooling as it moved away. When spraying aluminum, the peak temperature exceeded 80°C, above the recommended maximum operating temperature for PE that can become vulnerable to deformation under loading [6, 33]. The temperature dropped to an average value of about 40°C as the spray torch moved away and the substrates cooled. When spraying zinc (see Figure 3b), which has a much lower melting temperature than aluminum (420°C for zinc, 660°C for aluminum, see Table 1), the temperature rise was much less. It took longer for the substrate to heat up so that repeated passes of the spray produced a gradual increase in surface temperature, reaching a peak of approximately 45°C.

3.2.2 Samples at Elevated Temperatures

Metal coatings were also applied on polymer substrates that were preheated before the start of spraying. The goal was to raise the peak substrate temperature during spraying so that it approached the glass transition temperature of the polymer, making it soft enough for impacting particles to penetrate it. However, care had to be taken not to overheat the substrate and damage it.

Once spraying started the surface experienced a slight cooling due to the compressed air jet from the wire-arc system, followed by a sudden temperature rise as metal particles started to impinge on it (see Figure 4a). The peak temperatures were in the glass transition temperature range of PTFE (115 °C – 125 °C, see Table 1). When zinc was sprayed on PTFE the initial surface temperature was raised to 105 °C. In this case the surface was first cooled by impinging air and the surface temperature rebounded to 103°C when metal began to impinge on it. During the 10 passes of the zinc spray, the maximum surface temperature during each pass was in the range of 55-60 °C (see Figure 4b).

3.3 Adhesion Strength

3.3.1 Samples at Room Temperature

All pull tests resulted in an adhesive type of fracture, characterized by complete detachment of coatings from the substrate. Zinc coatings adhered to both PTFE and PE substrates, while aluminum adhered only to PTFE. Typically, each pass of the spray torch deposited a 37 ± 3 µm thick layer of metal so that 260 ± 20 µm thick coatings were deposited in 7 passes. No contiguous coating of aluminum could be applied on PE. Figure 5 shows measured coating adhesion strengths that were carried out on coatings 260 ± 20 μm thick. Zinc coatings deposited on smooth PTFE (R_a = 0.2 μm) had adhesion strength of about 0.4 MPa. **Coatings with such low adhesion strength values was also observed when arc spraying copper on CFRP [15] and plasma spraying of copper on CFRP [13]. Chen *et al.* [3] characterized the thermal performance of zinc sprayed Acrylonitrile Butadiene Styrene (ABS). The coatings in their study had bond strength values in the range of 0.5-2.5 MPa, which is comparable to the results obtained in the current study. Therefore, thick coatings could be developed despite the low adhesion strength values.**

Grit blasting the surface to increase roughness to 1.6 μm prior to coating doubled the adhesion strength. The same trend was observed with zinc coatings on PE substrates, where increasing surface roughness enhanced adhesion strength. **Ganesan *et al.* [13] observed similar kind of improvement in coating bond strength after grit blasting the polymer substrates prior to thermal spraying. Therefore, increased surface roughness promotes mechanical interlocking of the coating material with asperities in the surface and therefore increases adhesion strength.**

Aluminum coatings had a higher adhesion strength than zinc on smooth PTFE surfaces, over 0.7 MPa, and increasing surface roughness almost doubled that value. Figure 6 shows SEM cross-sections of zinc and aluminum coatings on both smooth (Figs. 6a and b) and rough (Figs. 6c and d) PTFE substrates. **It can be seen from Figs. 3a and 3b that the PTFE surface temperature when spraying with zinc was comparatively lower than while spraying with aluminum. As a result, the PTFE surfaces may not have softened enough, limiting the extent of interlocking**

of zinc particles with the substrate. Aluminum particles, by contrast, transferred more heat to the PTFE surfaces due to their comparatively high temperatures created by the exothermic oxidation of aluminum in air. This could have aided in softening the PTFE substrates to a greater extent, allowing Al particle penetration into it. This difference in the bonding line between Al-PTFE and Zn-PTFE can also be observed in Figs. 6a and 6b, where aluminum particle penetration seemed to have occurred to a greater extent than zinc.

In the rough substrates (Figure 6c and Figure 6d) there is evidence of penetration of metal into crevices in the substrates, which would enhance coating adhesion (see the areas outlined in Figure 6d). The extent of penetration in the smooth substrates (Figure 6a and Figure 6b) was comparatively less which resulted in coatings with lower adhesion strength. The size and shape of individual splats can also affect adhesion strength [19, 32, 34]. Figure 7 shows individual splats of aluminum and zinc splats after being sprayed on smooth PTFE at room temperature. 20-25 splats were chosen from each sample to calculate the equivalent diameter and circularity of the splats. Separation lines were drawn manually around each splat to calculate the equivalent diameter (*D*) and circularity of splats (*C*), respectively, as

$$D = 2\sqrt{\frac{A}{\pi}} \text{ and} \quad (1)$$

$$C = \frac{4\pi A}{P^2}, \quad (2)$$

where *P* and *A* are the perimeter and surface area of the splat, respectively [32]. The size of irregularly shaped splats was expressed in terms of *D*, which was defined as the diameter of a circle with the same area as the selected splat. Here the measured area corresponds to the area of a 2D image of the splat shape. Splat circularity lies between 0 and 1. A circularity of 1 corresponds to a perfectly circular splat, whereas splashed, fragmented and irregularly shaped splats typically have circularity values closer to zero. Molten zinc particles spread out significantly more than those of aluminum: the average equivalent diameter of zinc splats was measured to be 100 ± 10 µm, whereas that of aluminum splats was 60 ± 10 µm, even though zinc droplets in the spray were smaller (see Figure 2). Aluminum has a surface tension value approximately 30% higher than zinc (see Table 1) which would restrict spreading during impact. The circularity values of aluminum splats (0.41) were calculated to be higher than those of zinc (0.28), by about 45%, which also promotes adhesion strength [27]. **As a result, aluminum coatings on PTFE substrates were stronger than zinc coatings.**

Increasing surface roughness makes it easier for metal splats to adhere to surface asperities. Figure 8 shows zinc splats trapped in surface cavities on a PE substrate that were created by grit-blasting. Strong interlocking between the metal and rough polymer increases adhesion strength of the coating. **Similarly, Liu *et al.* [15, 35] observed excellent mechanical interlocking between grit blasted polymer matrix composites and zinc bond coating layer. Here, corundum powder was used for roughening the polymer substrate and it was found that by optimizing the grit blasting parameters, coatings with high bond strength could be achieved without damaging the substrate. Therefore, by increasing the roughness of polymer substrates the bond strength of the coatings could be enhanced significantly.**

Aluminum was found not to adhere to PE substrates irrespective of the surface roughness. Figure 9 show cross-sections of smooth (Figure 9a) and rough (Figure 9b) PE substrates respectively after seven passes of the spray torch. Aluminum particles adhered to both surfaces but did not form a contiguous coating. On the roughened PE (Figure 9b) substrates, the aluminum splats were observed to adhere to the asperities on the surface. Several more passes of the spray torch over the rough surface produced a thin, porous coating with thickness less than 50 μm and delamination at the corners of the samples. **A similar type of coating delamination was observed by Lie *et al.* [15] while arc spraying Cu onto carbon fiber reinforced thermosetting polyimide. This occurred due to the high melting point of Cu and low temperature resistance of polyimide.**

The failure of aluminum particles, unlike those of zinc, to penetrate PE during impact may be due to the high impact strength of PE (almost an order of magnitude greater than that of PTFE, see Table 2) and the low density of aluminum (one-third that of zinc, see Table 1). **As a result, cold spraying of Al on thermoplastics is generally carried out under high pressures and temperatures to provide greater impact force [10, 40]. However, in the current study, melting of the substrates of the substrates was observed when the stand-off distance was reduced to increase particle velocity. This was due to the increase in substrate temperature at low stand-off distances.** Additionally, Aluminum also has a higher melting point than zinc, which may have caused local melting and decomposition of PE under impacting particles, preventing adhesion. **It can also be seen in Figure 3a that the temperature of the polymer substrate during Al particle impact was consistently above 80 ^{0}C (maximum operating temperature of PE) throughout the spraying period. This could have also resulted in poor adhesion of aluminum onto PE substrates.**

3.3.2 Samples at Elevated Temperatures

Preheating smooth polymer substrates before the start of spraying enhanced adhesion strength by roughly the same amount as was achieved by grit blasting them to make them rougher. Figure 10 shows the measured adhesion strength of aluminum and zinc coatings on smooth polymer substrates both for those sprayed at room temperature and those sprayed on preheated substrates (95°C for PTFE and 55°C for PE).

Pre-heating the substrates makes them softer and allows impacting molten metal droplets to penetrate them before solidifying. The adhesion strength of zinc was approximately the same on both PTFE and PE substrates at room temperature. Preheating the substrates increased adhesion strength significantly since it promoted penetration of metal particles into the polymer. Figure 11a shows a cross-section through a 260 ± 20 µm thick zinc coating formed after 7 passes of the spray torch over a pre-heated PE surface showing good bonding at the metal-polymer interface. **A very similar bonding line as shown in Figure 11a was observed when Che *et al.* cold sprayed Cu on PEEK with a gas temperature above the T_g of PEEK. Here, the samples were not pre-heated but the high gas temperature (425 ^{0}C) combined with the extremely high velocity of Cu particles aided in achieving excellent adhesion with the substrates through particle embedment. However, in the current study, owing to the comparatively low particle velocity and the molten state of the spray particles in the wire-arc spray process [30], the substrates had to be pre-heated to promote such particle penetration into the substrate.** Figure 11b shows a cross-section through the interface after a single pass of the torch, showing deep penetration of metal particles up to a maximum depth of 20 µm. King *et al.* [36] previously observed copper particles penetrating to a depth of up 50 µm when a cold spray was used to deposit them on HDPE surfaces. A portion of the zinc particles in Figure 11b remained protruding above the surface so that they could serve as anchors for subsequent splats that coalesced with them. **When Ganesan *et al.* [8] cold sprayed copper particles on PVC, they observed similar kind of particle embedment phenomenon through FIB bisection of a**

copper particle on the substrate. It was found that such bonding mechanisms helped in developing thick copper coatings on PVC.

Figure 12 shows splats of zinc after impact on PE surfaces that were preheated to 55°C before spraying. Figure 12a shows a view from above, in which a splat appears to be partially buried in the polymer, showing how preheating promoted penetration of the metal into the substrate and good adhesion. Figure 12b shows splats that were sectioned using a focused ion beam to create a trench in the substrate. Splats can be seen both above and below the surface of the PE substrate, showing the deep penetration of the splats. **This kind of deep penetration provided excellent interlocking with the substrate. As a result, these initial set of splats served as an interlayer between PE and the subsequent molten Zn particles impacting the substrate, promoting overall adhesion of the coatings.** Some of the particles appear to be almost completely inside the substrate. **These particles could have travelled with a comparatively higher momentum, resulting in embedment of the whole particle in the substrate [30].**

The adhesion strength of aluminum on PTFE increases with substrate temperature, but it still did not adhere to PE. Figure 13 shows cross-sectional view of pre-heated PE substrates sprayed with aluminum after one (Figure 13a) and seven (Figure 13b) passes of the spray torch. The splats are flattened out and fragmented but show no evidence of particles piercing the substrate. Since there was no initial penetration there was no way for mechanical interlocking of the coating with the substrate to occur. Aluminum particles could also have caused local melting and decomposition of polymer substrates during impact due to the very high particle temperatures created by the exothermic oxidation of aluminum in air. Ashrafizadeh *et al.* [18] observed such decomposition at locations that were directly exposed to the high temperature flame while depositing Al-12Si on polyurethane substrates using flame spraying.

4 CONCLUSIONS

Coatings of aluminum and zinc were applied on two thermoplastic materials, PE and PTFE, using electric wire-arc spraying. Single splats of metal were observed after impact to understand the interaction of molten metal droplets (Al and Zn) with polymer substrates. Substrate roughness was increased using grit blasting. The temperature of the polymer substrates was monitored during spraying to understand how it affects the adhesion of metal particles.

Zinc coatings, about 260 μm thick, formed on both polymer substrates irrespective of their surface roughness. Increasing surface roughness significantly enhanced adhesion strength since it promoted mechanical interlocking of the metal with surface asperities. Increasing the initial substrate temperature so that the maximum substrate temperature during spraying reached the glass transition temperature of the polymer also enhanced adhesion strength. Individual zinc splats were observed to be buried deep inside heated polymer substrates.

Aluminum adhered only to the PTFE but not the PE. Aluminum particles have low density and therefore may not have enough momentum to penetrate PE, which has a much higher impact strength than PTFE. It is also possible that impacting droplets of aluminum, which have a higher melting point than zinc, caused localized melting of the substrate upon impact and therefore could not flow into surface cavities and freeze, which would have led to mechanical bonding.

5 CONFLICT OF INTERESTS

The authors of this work declare that they have no conflict of interests regarding the publication of this paper.

6 ACKNOWLEDGMENTS

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8 TABLES

Table 1: Properties of spray materials [37,38,39]

Metal	Density (kg/m^3)	T_m (^oC)	Surface Tension at Melting Point (Nm^{-1})	Specific Heat (J/kg-K)
Aluminum	2700	660	0.9	1180
Zinc	7200	420	0.65	427

Table 2: Properties of polymer substrate materials [23, 25, 26, 27]

	Density (kg/m^3)	T_m (^0C)	Glass-transition temp. (^oC)	Thermal Diffusivity (mm^2/s)	Specific Heat (J/kg-K)	Impact Strength (J/m)	Elastic Storage Modulus at 1 Hz (MPa)
PTFE	2200	320-330	115-125	0.12	970	186.8	1377
PE	900	125-135	~75	0.27	1900	896.8	1938

9 LIST OF FIGURE CAPTIONS

Figure 1: Schematic diagram of experimental apparatus

Figure 2: SEM images of particles of (a) aluminum (mean particle diameter d_{50} = 78.6 µm) and (b) zinc (d_{50} = 61.3 µm) captured by spraying into a water bath

Figure 3: Temperature variation of substrates during 10 passes of a wire-arc spray torch over a PTFE surface initially at room Temperature when spraying (a) aluminum and (b) zinc

Figure 4: Temperature variation of substrates during 10 passes of a wire-arc spray torch over (a) a PTFE surface initially at 95°C sprayed with aluminum and (b) a PE surface initially at 55°C coated with zinc. The initial temperature values of the substrates are labelled

Figure 5: Adhesion strength of aluminum and zinc coatings on rough and smooth polymer substrates. Aluminum coatings did not adhere to PE surfaces

Figure 6: Cross sectional view of (a) bonding line between zinc coating and smooth PTFE, (b) bonding line between aluminum coating and smooth PTFE, (c) zinc coating on rough PTFE and (d) aluminum coating on rough PTFE substrates. Areas of mechanical interlocking are outlined in (c)

Figure 7: Single splats of (a) zinc and (b) aluminum sprayed on a smooth PTFE surface at room temperature.

Figure 8: SEM image of a zinc splat trapped in the asperities of a rough PE substrate

Figure 9: Cross sectional view of PE substrates on which aluminum was sprayed. The surfaces were (a) smooth and (b) rough. The surfaces are shown inclined to the

horizontal so that both the coated surface and the cross-section through the substrate can be seen

Figure 10: Adhesion strength of aluminum and zinc coatings on polymer substrates that were initially either at room temperature or preheated (initial temperature 95°C for PTFE, 55°C for PE). Aluminum coatings did not adhere to PE surfaces

Figure 11: Cross sectional view of preheated PE substrates on which zinc was sprayed. (a) contiguous coating formed after 7 passes of the spray torch and (b) individual particles deposited after 1 pass of the spray torch

Figure 12: Single splats of zinc on PE preheated to 55°C (a) viewed from above and (b) section through substrate made using a focused ion beam (FIB)**, revealing zinc penetration into PE substrate.**

Figure 13: Cross sectional view of preheated PE substrates on which aluminum was sprayed. (a) after 1 pass and (b) after 7 passes of the spray torch

Credit Author Statement

Sudarshan Devaraj: Conceptualization; Data curation; Formal analysis; Investigation; Validation; Visualization; Roles/Writing - original draft

Bobby Anand: Conceptualization; Data curation; Investigation; Methodology; Software

Michael Gibbons: Conceptualization; Methodology; Resources; Writing - review & editing

André McDonald: Conceptualization; Investigation; Methodology; Project administration; Resources; Supervision; Writing - review & editing

Sanjeev Chandra: Conceptualization; Funding acquisition; Investigation; Methodology; Project administration; Resources; Supervision; Writing - review & editing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

HIGHLIGHTS:

- **Aluminum and zinc coatings, about 260 ± 20 μm thick, were successfully deposited on polytetrafluoroethylene (PTFE) using twin wire-arc spray spraying.**
- **The adhesion strength of zinc coatings on PTFE and PE improved by both pre-heating and grit blasting the polymer substrates prior to thermal spraying.**
- **Aluminum coatings could only be deposited on PTFE and not on polyethylene (PE) regardless of the grit blasting and pre-heating processes.**

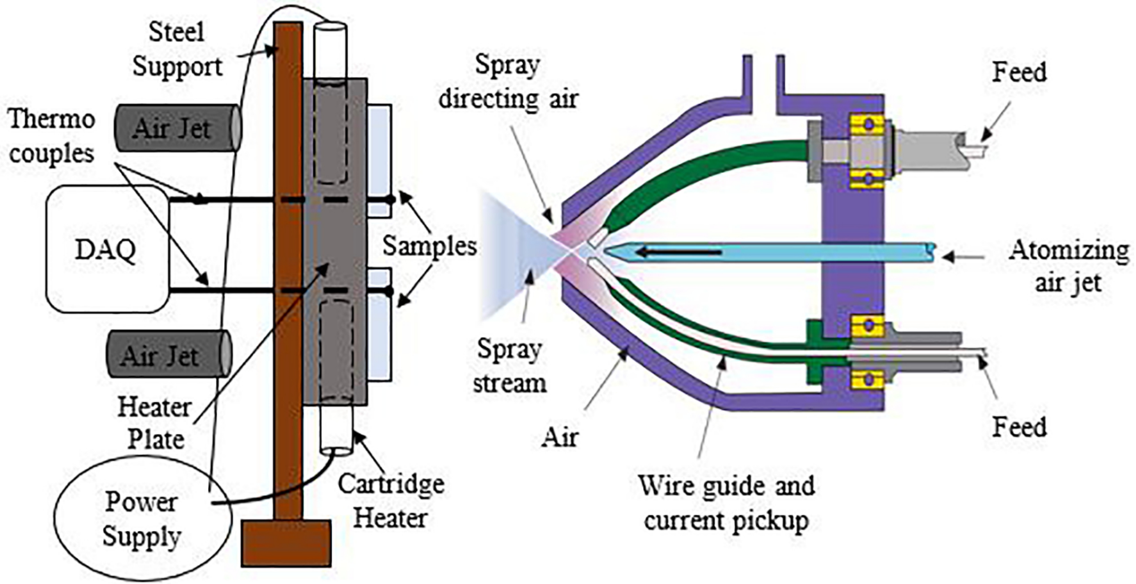

Steel Support
Thermo couples
Air Jet
DAQ
Air Jet
Heater Plate
Power Supply
Cartridge Heater
Samples
Spray directing air
Spray stream
Air
Wire guide and current pickup
Feed
Atomizing air jet
Feed

Figure 1

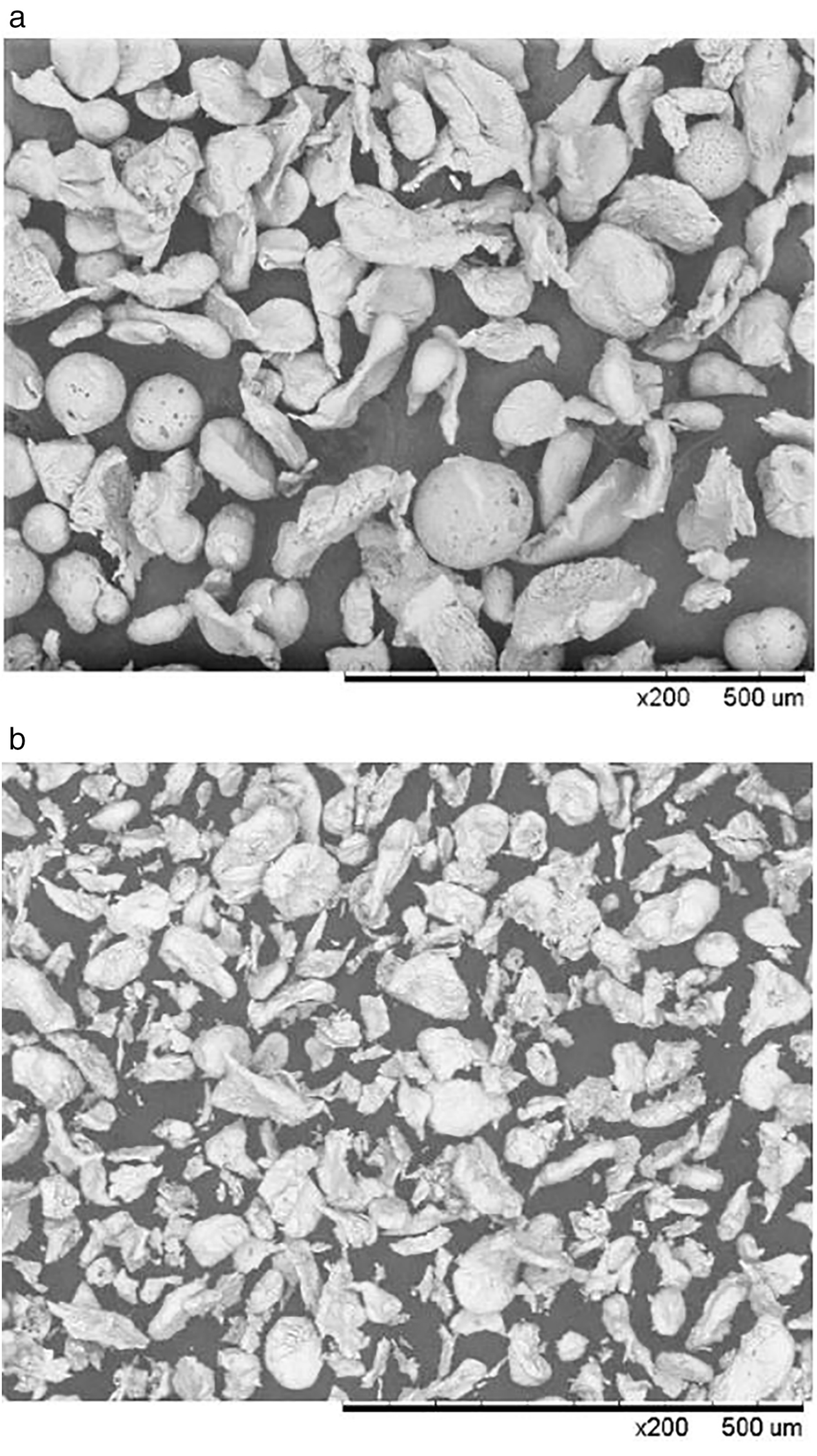
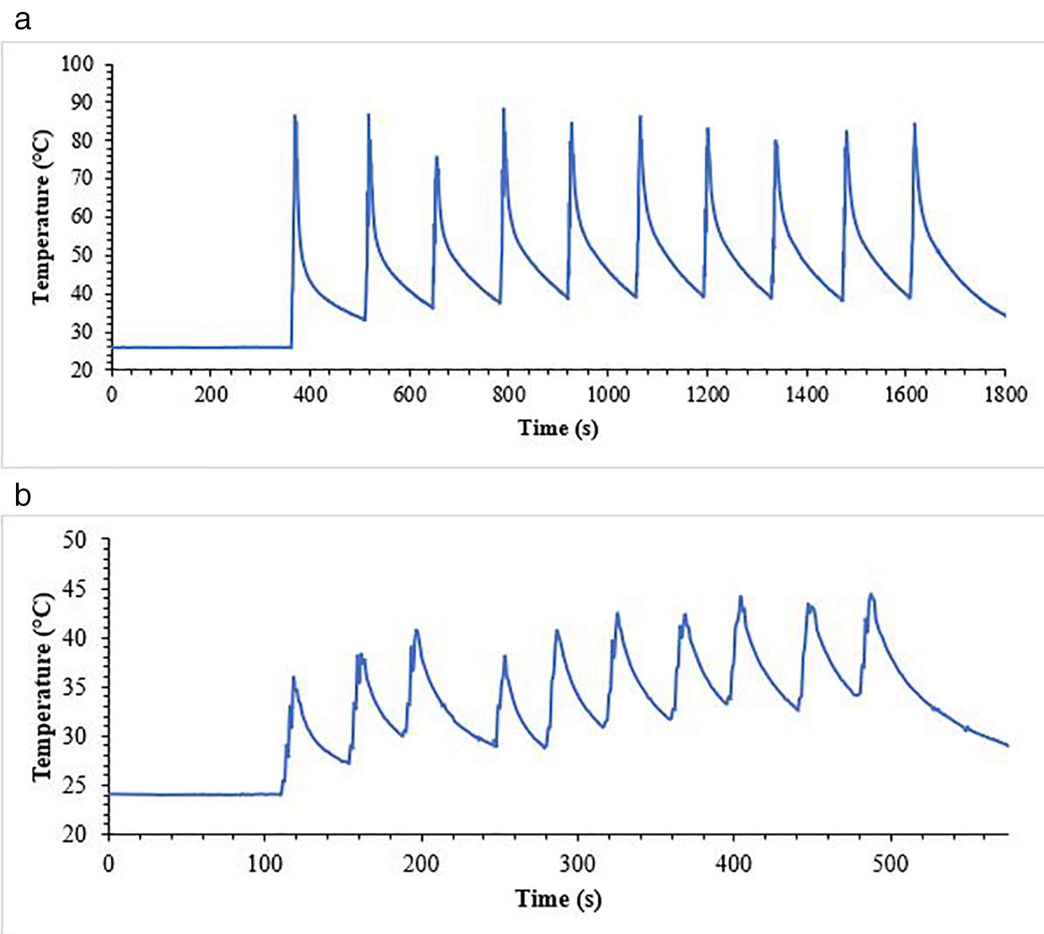


Figure 2

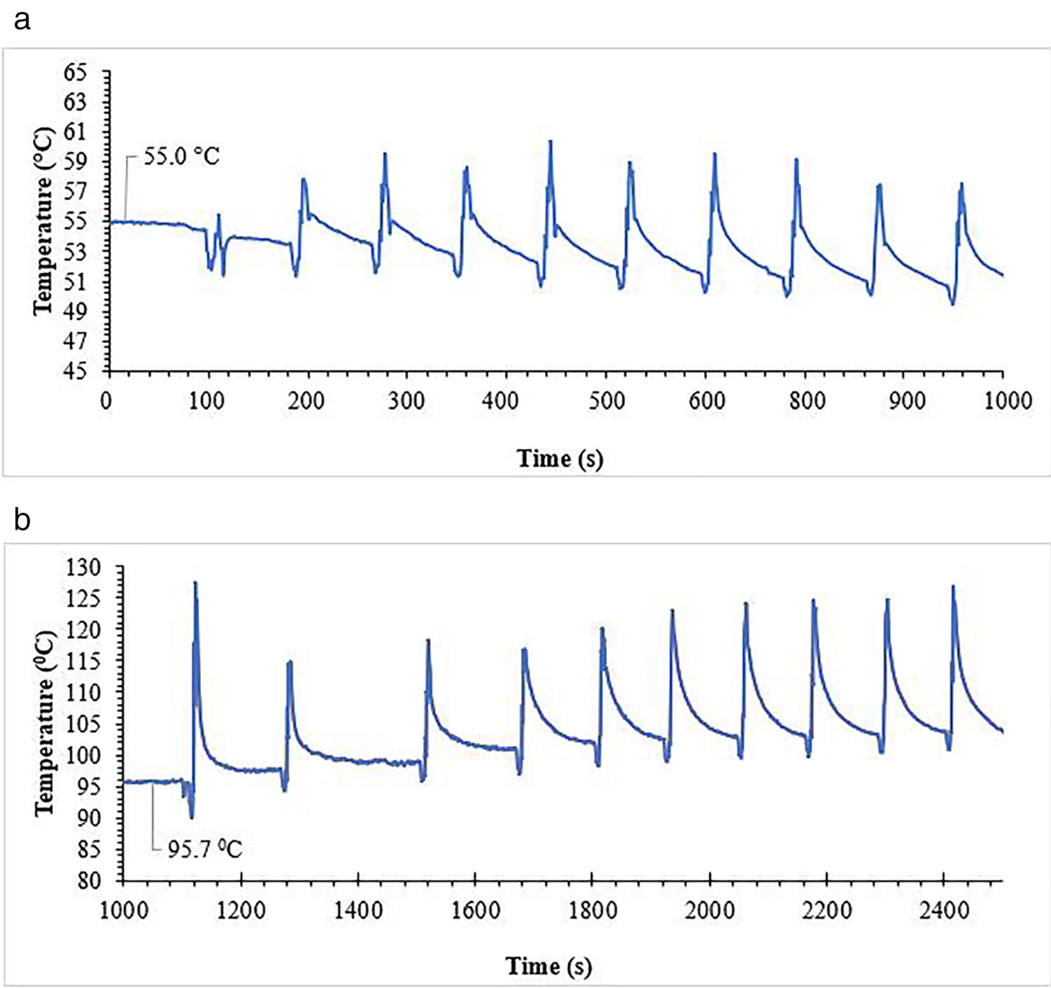
a



a
100
90
80
70
60
50
40
30
20
Temperature (°C)
0
200
400
600
800
1000
1200
1400
1600
1800
Time (s)
b
50
45
40
35
30
25
20
Temperature (°C)
0
100
200
300
400
500
Time (s)

Figure 3

a



Temperature (°C)
55.0 °C
Time (s)
65
63
61
59
57
55
53
51
49
47
45
0
100
200
300
400
500
600
800
800
900
1000
Temperature (⁰C)
95.7 ⁰C
Time (s)
130
125
120
115
110
105
100
95
90
85
80
1000
1200
1400
1600
1800
2000
2200
2400

Figure 4

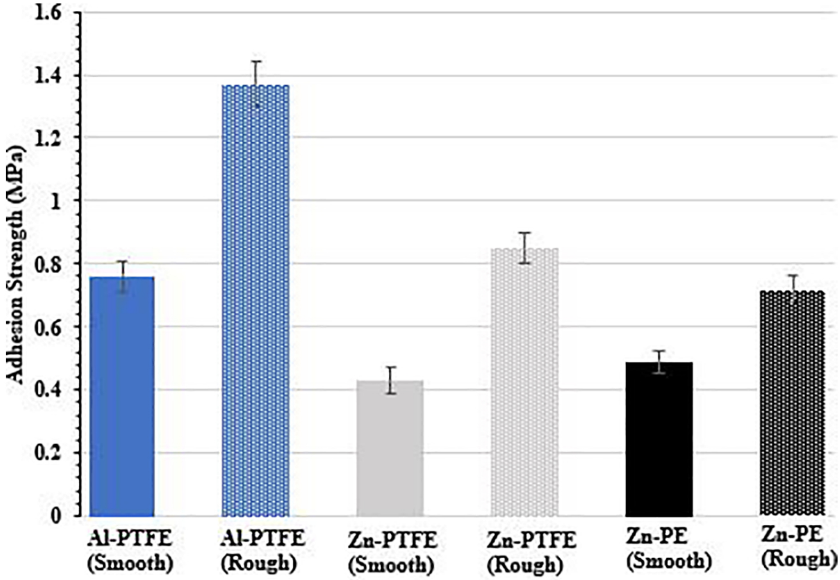

1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Adhesion Strength (MPa)
Al-PTFE (Smooth)
Al-PTFE (Rough)
Zn-PTFE (Smooth)
Zn-PTFE (Rough)
Zn-PE (Smooth)
Zn-PE (Rough)

Figure 5

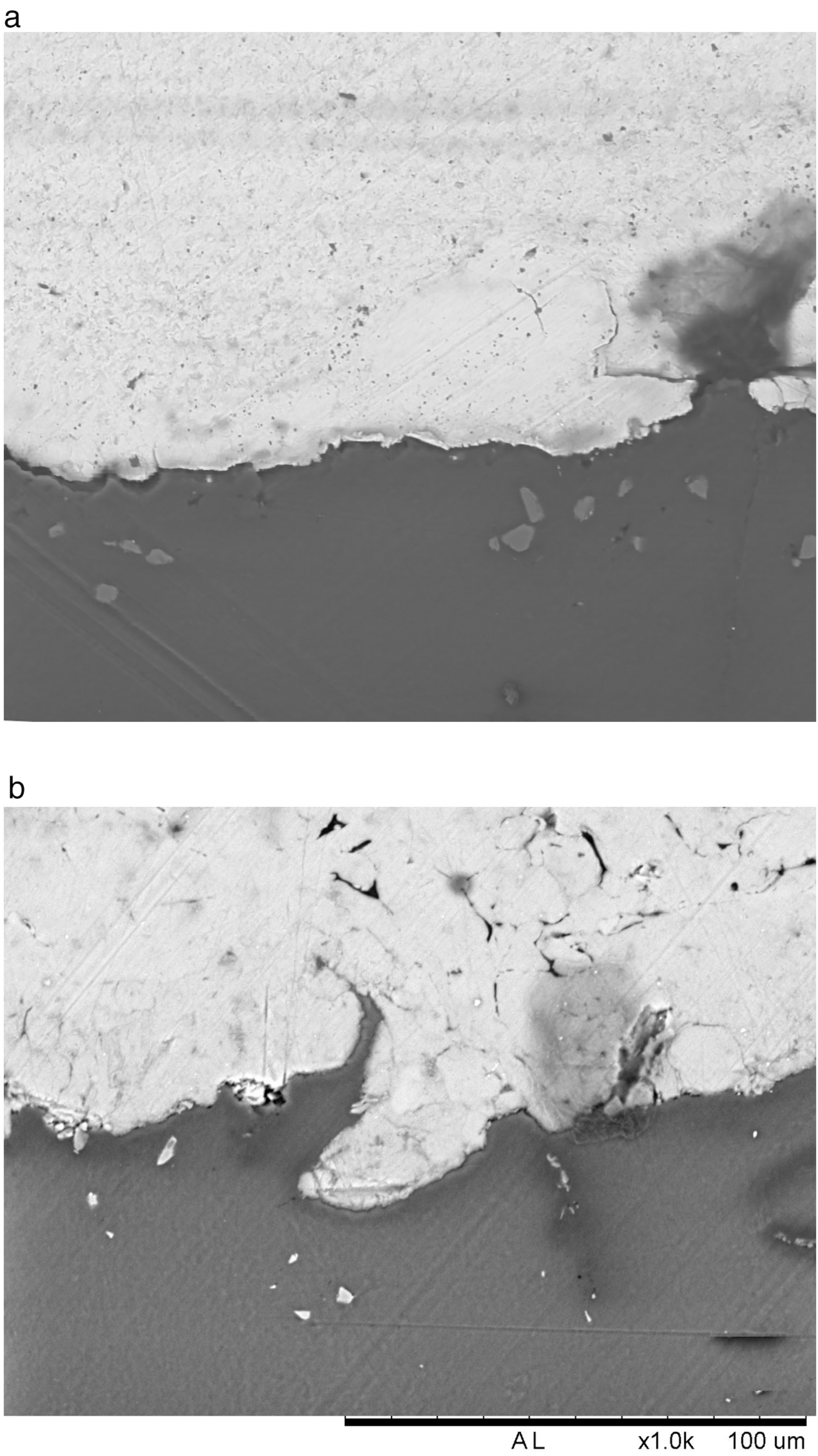
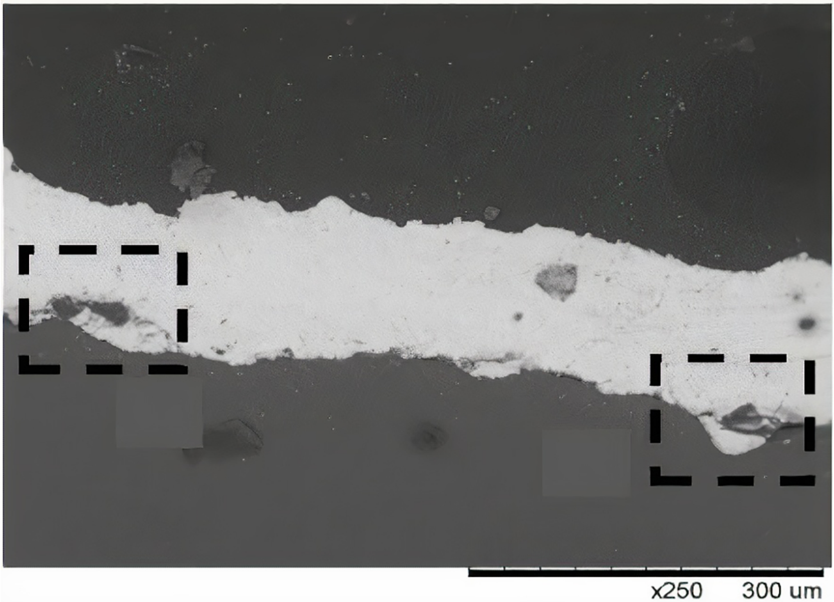


Figure 6ab

c



d

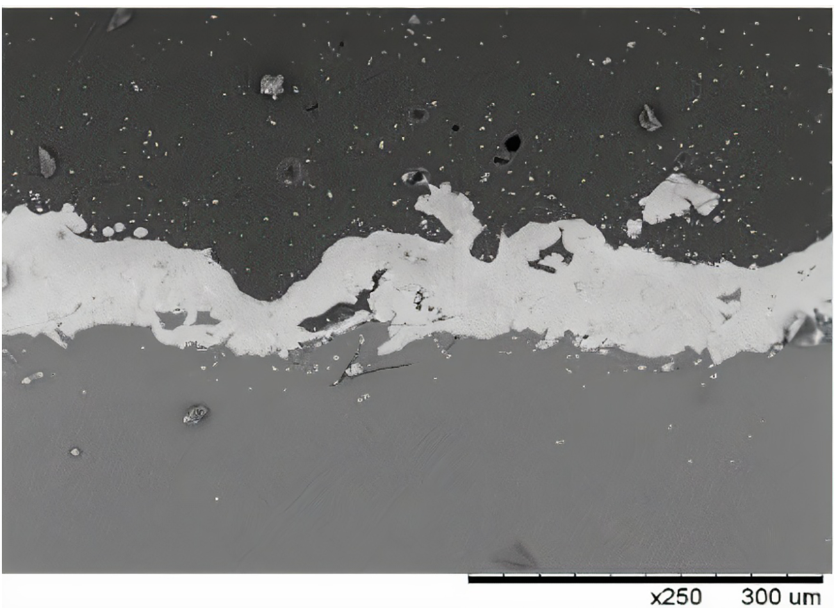
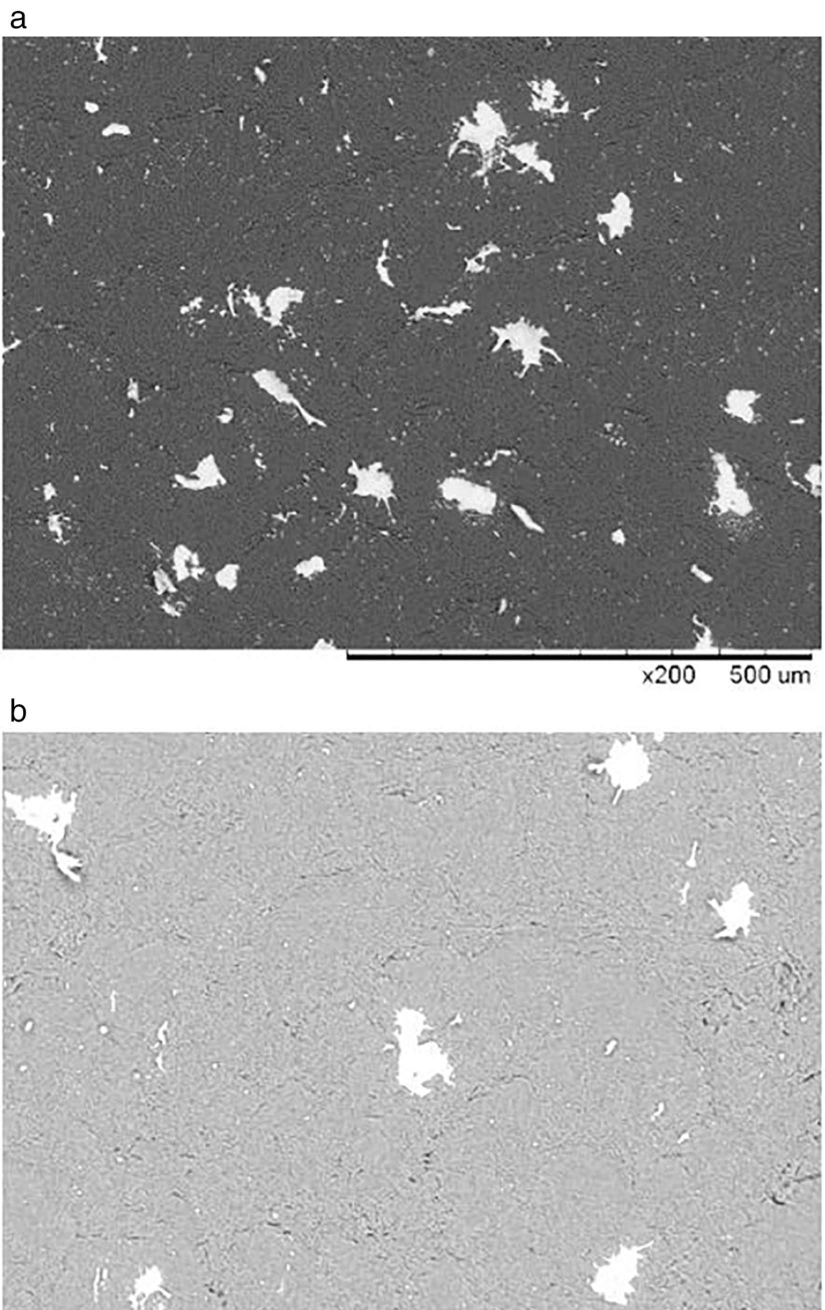


Figure 6cd



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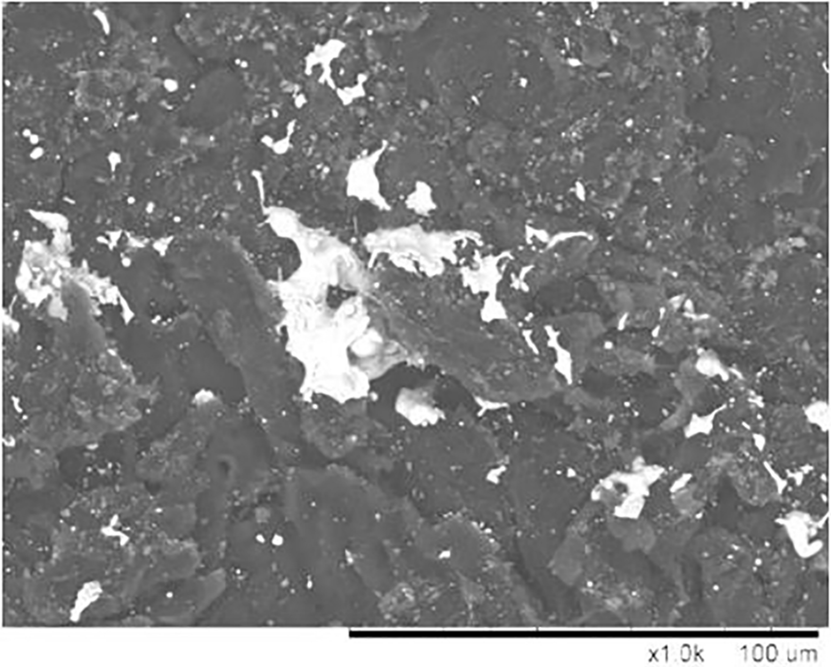


Figure 8

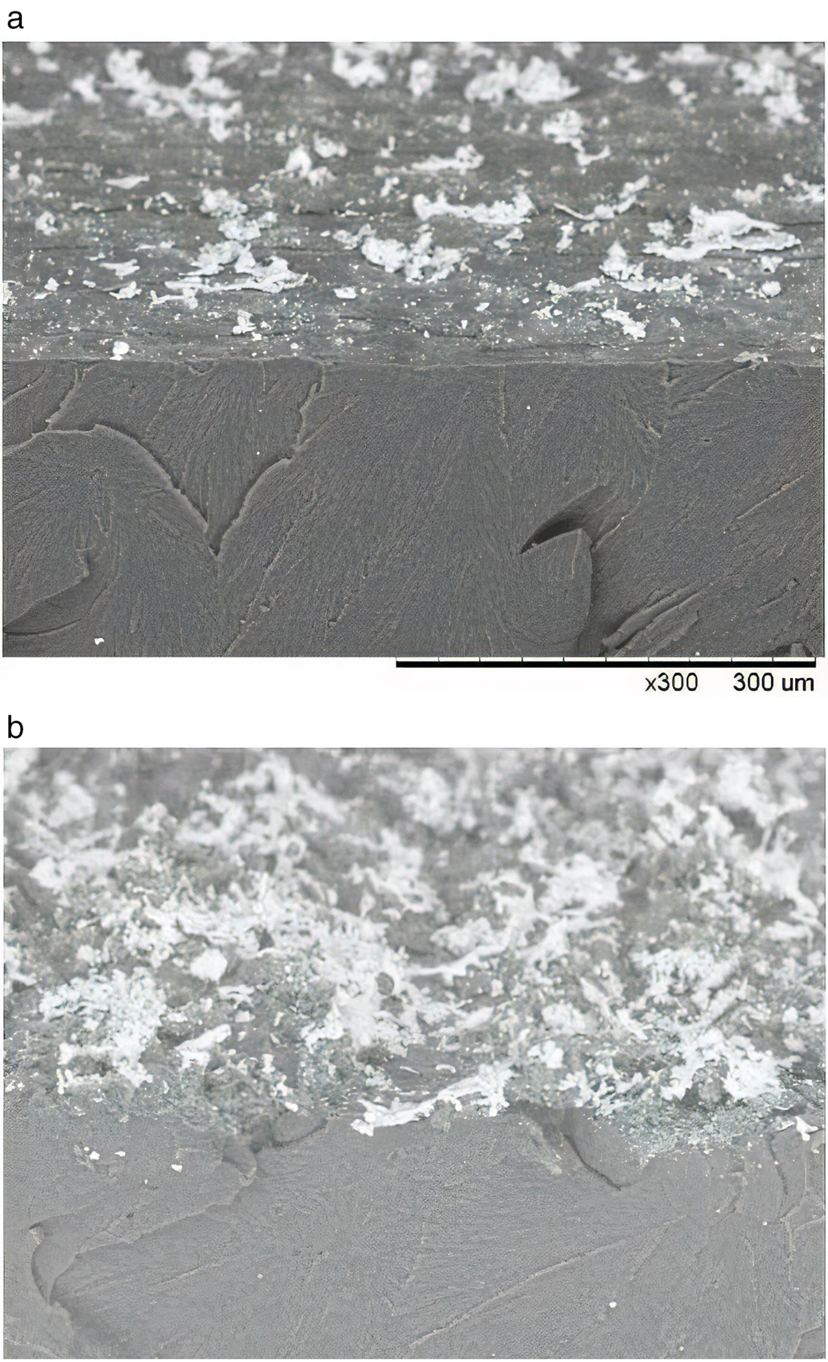


Figure 9

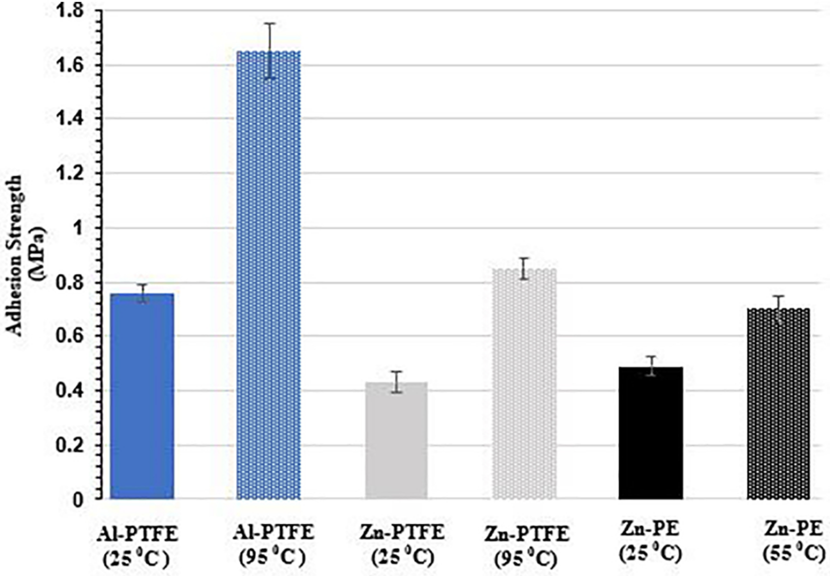

1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Adhesion Strength (MPa)
Al-PTFE (25 ⁰C)
Al-PTFE (95 ⁰C)
Zn-PTFE (25 ⁰C)
Zn-PTFE (95 ⁰C)
Zn-PE (25 ⁰C)
Zn-PE (55 ⁰C)

Figure 10

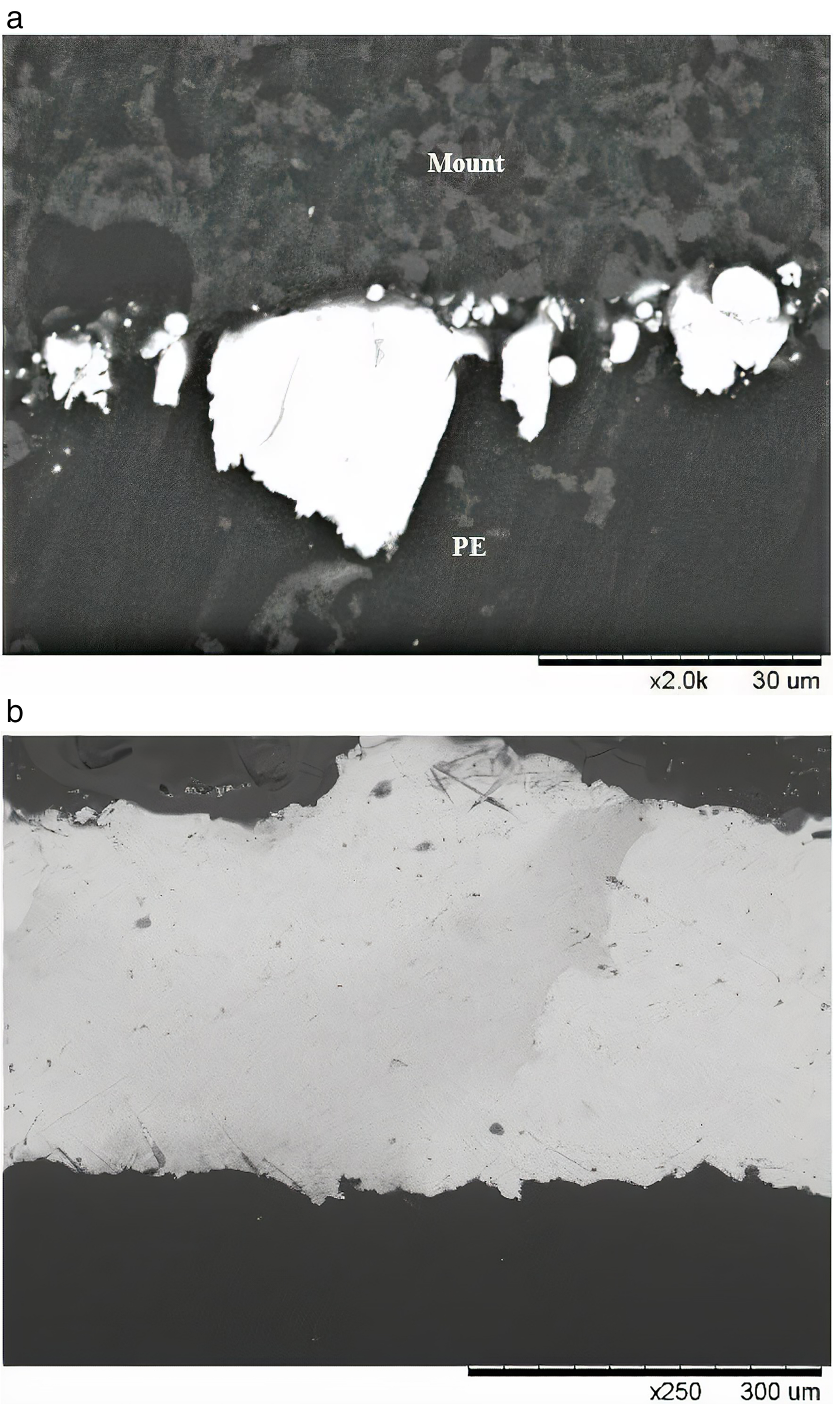
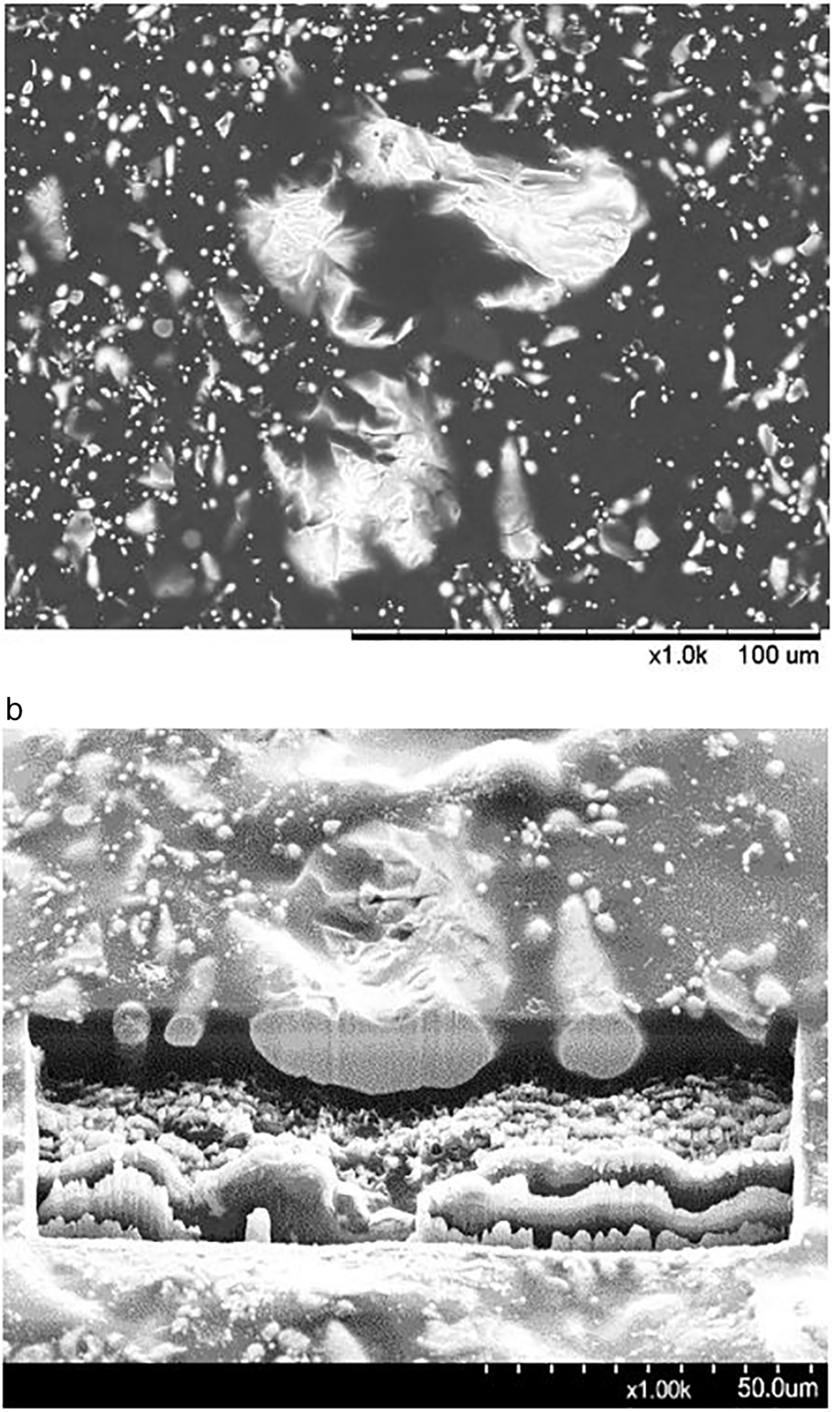


Figure 11

a


b

Figure 12

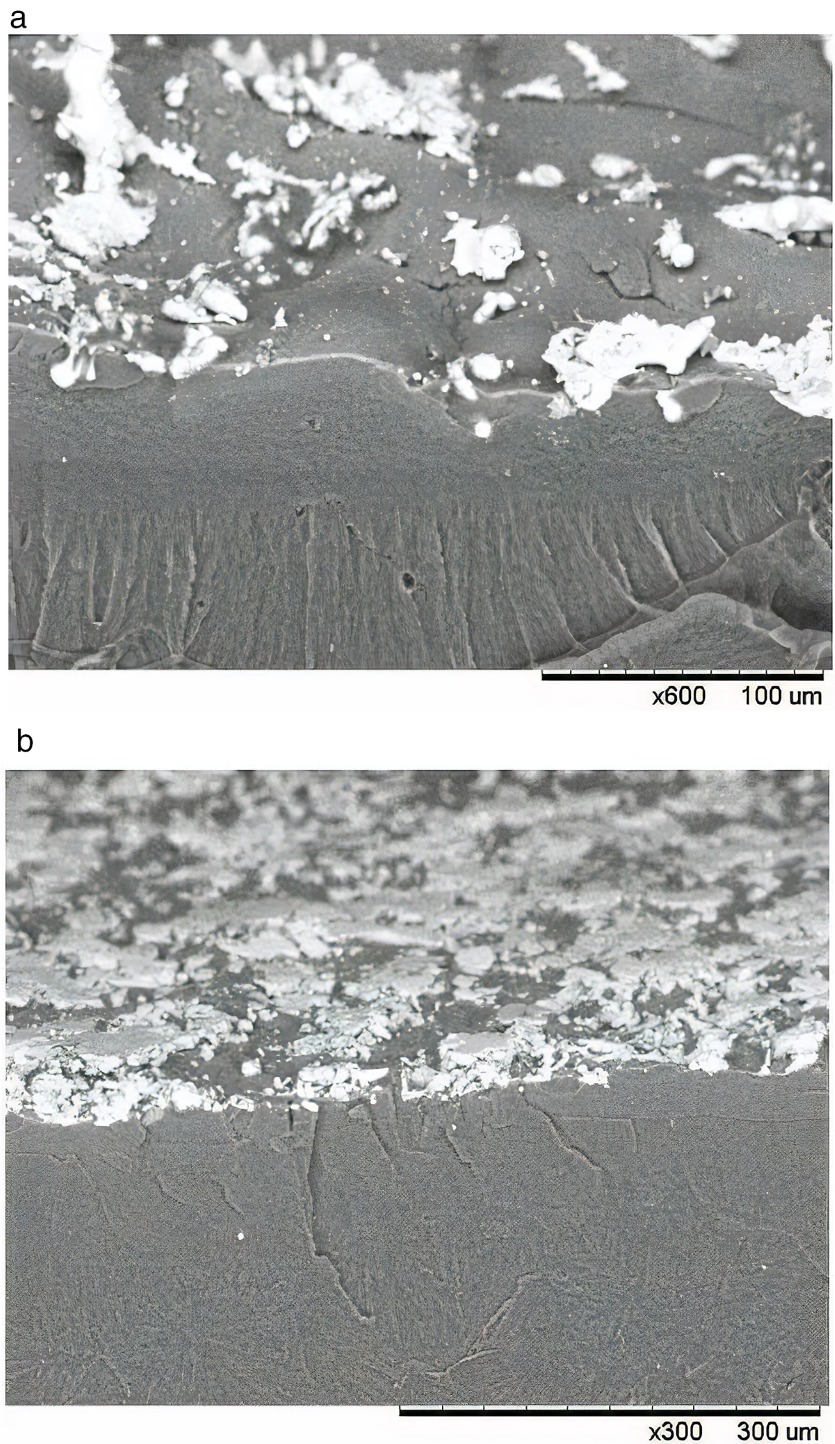


Figure 13