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Adhesive/Cohesive Properties of Thermally Sprayed Functionally Graded Coatings for Polymer Matrix Composites

Milan Ivosevic, Richard Knight, Surya R. Kalidindi, Giuseppe R. Palmese, and James. K. Sutter

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High-velocity oxyfuel (HVOF) sprayed polyimide/WC-Co functionally graded (FGM) coatings with flame-sprayed WC-Co topcoats have been investigated as solutions to improve the solid-particle erosion and oxidation resistance of polymer matrix composites (PMCs) in the gas flow path of advanced turbine engines. Porosity, coating thickness, and volume fraction of the WC-Co phase retained in the graded coating architecture were determined using standard metallographic techniques and computer image analysis. The adhesive bond strength of three different types of coatings was evaluated according to ASTM D 4541. Adhesive/cohesive strengths of the FGM coating were measured and compared with those of pure polyimide and polyimide/WC-Co composite coatings and also related to the tensile strength of the uncoated PMC substrate perpendicular to the thickness. The FGM coatings exhibited lower adhesive bond strengths (~6.2 MPa) than pure polyimide coatings (~8.4 MPa), and in all cases these values were lower than the tensile strength (~17.6 MPa) of the reference uncoated PMC substrate. The nature and locus of the failures were characterized according to the percent adhesive and/or cohesive failure, and the interfaces tested and layers involved were analyzed by scanning electron microscopy.

Keywords adhesion/cohesion, functionally graded coatings, thermally sprayed polymers

1. Introduction

The successful integration of high-temperature polymer matrix composites (PMCs) into jet engines requires that key long-term performance characteristics such as solid-particle erosion resistance and thermomechanical fatigue (TMF) behavior be addressed. Even with significant benefits such as weight savings, improved strength, reduced part counts, and reduced manufacturing costs, the successful application of PMCs into the gas flow paths of advanced turbine engines is still limited by their poor erosion resistance. There is, however, little published information describing solutions to this erosion problem on polymer matrix composites (Ref 1). Erosion-resistant coatings are needed to protect the composite materials, at least through the first overhaul interval, and preferably over the full lifetime of the component. In addition, components used in turbine gas flow paths must exhibit an acceptable surface finish to ensure good aerodynamic performance. The overall goal of this work was to develop thermally sprayed functionally graded (FGM) erosion/oxidation resistant coatings for PMC substrates. The approach was to grade the coating composition from pure polyimide, similar to the matrix of the PMC substrate on one side, to 100% WC-Co on the other (Ref 2). A 100% WC-Co outer layer should provide improved erosion and oxidation protection to the substrate. The thermosetting polyimide-coating matrix should help manage the differences in coefficient of thermal expansion (CTE) between WC-Co and the PMC substrate material and improve the TMF properties of the coating/substrate system. Results reported focus on coating microstructure and aspects of the adhesion and/or cohesion properties of the FGM coatings produced using a combination of high-velocity oxyfuel (HVOF) and powder flame spray processes.

2. Background

The limited work reported on the thermal spray deposition of erosion-resistant coatings on fiber-reinforced polymer composites (Ref 3-5) almost exclusively used metallic (zinc, nickel, or aluminum) bondcoats or polymeric (polyamide, polyimide, or poly ether ether ketone) layers to enhance the adhesion of wear-resistant topcoats (typically, carbides, borides, or nitrides) to PMC substrates. For applications subject to thermal fatigue or thermomechanical fatigue, however, this may be a limitation caused by the large differences in CTE within the overall coating/substrate system. Work on the plasma spraying of epoxy-based materials (Ref 6, 7) reported some difficulty in obtaining satisfactory coating buildup and properties of thermosetting polymeric coatings. It was reported that external substrate preheating might enhance the deposition behavior and curing reaction during the thermal spraying of thermosetting polyimide materials. Preliminary proof-of-concept evaluations resulting in the

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M. Ivosevic, R. Knight, S.R. Kalidindi, and **G.R. Palmese,** Drexel University, Philadelphia, PA; and **J.K. Sutter,** NASA-Glenn Research Center at Lewis Field, Cleveland, OH. Contact e-mail: knightr@coe.drexel.edu.

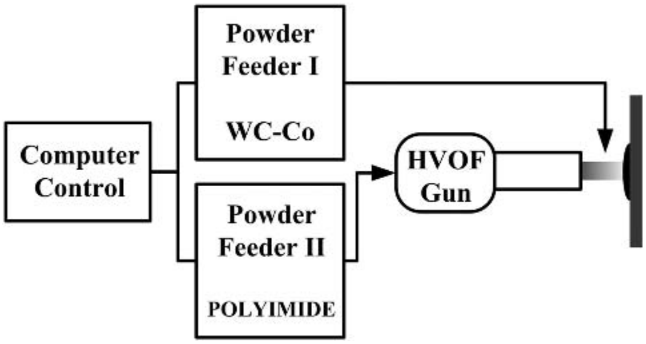

Fig. 1 Simultaneous internal/external powder feeding of the polyimide and WC-Co feedstocks

successful deposition and buildup of pure polyimide and polyimide/WC-Co powders onto electrically preheated PMR-15 substrates were previously reported (Ref 2). Improved substrate preheating systems were subsequently developed and used during this work.

The potential benefits of using polymer matrix coatings filled with commercial or nanosized ceramic (e.g., silica or alumina) reinforcements or fillers has been reported by a number of authors (Ref 8-10). The high velocities and nonuniform velocity distributions of thermal spray jets, in combination with variations in particle size, density, and morphology can, however, result in significant segregation when dissimilar materials are cosprayed. This represents a serious challenge when the desired feedstock materials have significant differences in density, as was the case for the two materials used in this work, polyimide and WC-Co, which have densities of 1.39 and 12.5 g/cm^3, respectively. Consequently, spraying techniques that minimized material segregation were a key requirement. One approach considered for minimizing material segregation was dry ball milling to produce a "composite" feedstock, with the ceramic phase mechanically embedded into the polymer component. Ball milling of the polyimide and WC-Co powders was investigated here; however, as reported previously (Ref 2), little or no embedding of the harder WC-Co particles into the softer, yet somewhat brittle, thermosetting polyimide particles was obtained.

An alternative approach to minimize material segregation was investigated in which a powder feeding configuration that allowed simultaneous internal and external feeding of the two materials, as shown in Fig. 1. External feeding of the much denser WC-Co component and internal feeding of the polyimide enabled a balance between the differences in momentum and kinetic energy of the two feedstock materials to be established. Moreover, this configuration also helped to minimize the differences in heating of the polymer and cermet feedstocks. Internal feeding of the polyimide material with a much lower thermal conductivity (~0.2 W/m · K) afforded longer residence times within the HVOF jet than those experienced by the externally fed, higher thermal conductivity (~100 W/m · K) WC-Co.

A 100% WC-Co outer layer, or topcoat, was sprayed using a flame-powder spray system because the high kinetic energy and momentum of the HVOF sprayed WC-Co particles, with internal powder injection, was found to be sufficient to remove previously deposited material from the substrate. The significantly lower particle speeds (up to only ~80 m/s) of flame spray compared with HVOF (with particle speeds up to 1000 m/s) resulted in the successful deposition of pure WC-Co material without removing or thermally decomposing the previously HVOF-deposited polyimide/WC-Co composite layers from the substrate.

Table 1 HVOF spray parameters used to deposit pure polyimide and various ratios of polyimide/WC-Co coatings on T650-35/PMR-15 composite substrates

HVOF spray parameter	Value
Spray distance, m	0.15
Polyimide feed rate, g/min	2-9
WC-Co feed rate, g/min	20-50
Carrier gas	Ar
Carrier gas flow rate, m^3/s	0.5×10^{-4}
H_2:O_2 ratio	0.4-0.5
H_2 and O_2 flow rates, m^3/s	3×10^{-3}/6-7 $\times 10^{-3}$
Surface speed, m/s	0.11
Substrate preheat temp., °C	230-340

3. Experimental Approach

PMR-II is a thermoset polyimide selected as the matrix material for the proposed FGM coatings. Imidized PMR-II molding compound, produced by Maverick Corp. (Cincinnati, OH), was mechanically crushed and cryo-ground (Shamrock Technologies, Inc., Newark, NJ) to produce a powder that flowed well, with a particle size distribution in the range of −100 +20 μm, suitable for HVOF spraying. A WC-Co powder—Amperit 515.0 (H.C. Stark, Inc.)—with a particle size range of −22.5 +5.6 μm was selected as the reinforcing/filler material. PMC substrates were 25 × 75 × 3 mm (1 × 3 × ⅛ in.) coupons of carbon-fiber (T650-35/8HS/3K weave) reinforced polymer matrix (PMR-15) composite material. Prior to spraying, the T650-35/PMR-15 substrates were lightly grit blasted using 250 μm (60 mesh) Al_2O_3 grit and cleaned.

Pure thermosetting polyimide coatings and polyimide/WC-Co composite coatings were sprayed using a Stellite Coatings, Inc. (Gosher, IN), Jet Kote II HVOF combustion spray system, using hydrogen as fuel gas. All the coatings were sprayed using the spray parameters summarized in Table 1.

Coating thicknesses obtained were in the range 300-600 μm (12-24 mils). A 100% WC-Co outer layer, or topcoat, was sprayed using a UTP UNI-Spray-Jet flame-powder spray system (Houston, TX), again using hydrogen as the fuel gas. The flame spray parameters are summarized in Table 2.

Spraying of the graded coating structures required reliable, repeatable, simultaneous feeding of two dissimilar materials, WC-Co and PMR-II polyimide. A LabVIEW®-based computer-controlled system was developed and used to simultaneously control two identical Praxair Model 1207 volumetric powder feeders (Indianapolis, IN) (Fig. 1). Electric strip heaters (Omega type PT 502/120, Stamford, CT) were used as external heat sources in contact with the rear face of the substrate, together with a hot air gun directed at the front face (Ref 10). Preheating was used only while spraying the pure polyimide and polyimide/WC-Co layers, not during the flame spraying of the WC-Co topcoats.

Porosity, coating thickness, and volume fraction of WC-Co filler retained in the coatings were determined using standard

Table 2 Typical flame spray parameters used for spraying pure WC-Co topcoats over predeposited polyimide/WC-Co layers

Flame spray parameter	Value
Spray distance, m	0.08
WC-Co feed rate, g/min	70
Carrier gas	Ar
Gas pressure—H_2, MPa	0.138
Gas pressure—O_2, MPa	0.242
Gas pressure—cooling air, MPa	0.069
Surface speed, m/s	<0.11
Substrate surface temperature, °C	15

Table 3 Types of coating evaluated by tensile adhesion testing

	Coating designation	Composition
I	Pure polyimide coating	A + B
II	Two-layer coating	A + B + C
III	Three-layer coating	A + B + C + D

metallographic techniques—sectioning, mounting, and polishing—and computer image analysis using Scion Image software (Frederick, MD). The adhesive bond strength of the coatings was determined according to ASTM D 4541 by measuring the greatest normal tensile force that the coatings could withstand. A schematic illustration of the pull-off test method is shown in Fig. 2.

The test conditions used were as follows:

- Self-aligning sample fixtures adapted for laboratory use on an Instron 5800R mechanical testing machine (Model 58R1127 in conjunction with Instron Merlin software)
- Temperature and relative humidity of 20 °C and 65%
- 13 mm aluminum pull stubs (type PS-25, M.E. Taylor Engineering, Inc., Brookeville, MD) prepared in accordance with the ASTM D 2651 guide for the preparation of metal surfaces for adhesive bonding
- 3M type DP-460 off-white adhesive, with a curing time of 60 min at a temperature of 60 °C

The bearing ring was located concentrically around the loading fixture on the coating surface (Fig. 2). The adhesive/cohesive strengths of three different types (Table 3) of coatings were measured and compared based on the maximum indicated load and the surface area stressed. Six samples of each coating type were tested, and the mean value of the results reported.

A, carbon-fiber reinforced T650-35/PMR-15 substrate;
B, pure PMR-II polyimide coating layer;
C, WC-Co/polyimide composite coating layer;
D, pure WC-Co topcoat

A one-dimensional analysis of variance (ANOVA) test was conducted to statistically evaluate differences between the three coating systems, including the statistical significance of these differences.

The nature and locus of the failures were characterized according to the percent of adhesive and cohesive failures. The surfaces of the "as-tested" samples were subsequently analyzed by scanning electron microscopy (SEM) using an Amray Model 1830 SEM.

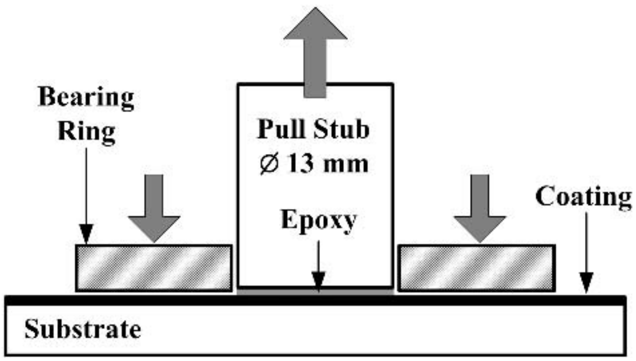

Fig. 2 Schematic illustration of the ASTM D 4541 standard pull-off test method

4. Results and Discussion

An important first step in this work was the development of HVOF spray parameters for depositing the pure polyimide matrix material onto PMC substrates, due to the reported difficulty in obtaining satisfactory initial coating buildup (Ref 2). An adherent pure polyimide coating (region B, Fig. 3) was obtained after extensive parameter development and understanding of the substrate preheating requirements. These coatings exhibited good adhesion and clean coating/substrate interfaces with little or no apparent debonding.

A significant level of porosity—the large black areas within region B of Fig. 3—was observed in the pure polyimide coating. The high void level (~26%) may have been due to gas evolution from residual condensation by-products or during the crosslinking reaction (the onset of polymerization of the oligomer end-groups) that began above ~280 °C. Outgassing of the PMC substrate material may also have contributed to the excessive porosity observed, even though the substrates were vacuum dried at ~120 °C for ~2 days and stored in a desiccator prior to spraying. Since gas evolution during crosslinking is a function of the polyimide chemistry and imidization kinetics, this problem may be addressed in the future by further studying these relations.

Two- and three-layer FGM polyimide/WC-Co coating microstructures are shown in Fig. 4 and 5. Image analysis of the WC-Co/polyimide layers (region C) shown in Fig. 4 and 5 indicated that the composite layer typically had the following composition: 46% polyimide matrix, 26% WC-Co filler, and 28% voids/porosity.

Neglecting voids, this indicated that the relative proportions of the polyimide matrix and WC-Co filler were 58 and 42%, respectively. The flame sprayed WC-Co topcoat layers also appeared to be much more porous (~16%) than expected (Fig. 5) due to insufficient kinetic energy of the flame sprayed WC-Co material, which is typically deposited using HVOF. The high porosity level could be problematic from the perspective of potential coating applications in propulsion environments because hot environmental gases could enhance the oxidation rate of the coating and substrate matrix materials. In addition, a rough and porous topcoat is likely to provide less erosion protection than the same coating if it were fully dense; however, erosion and oxidation performance of these coating systems exceeds the scope of this paper and will be reported separately.

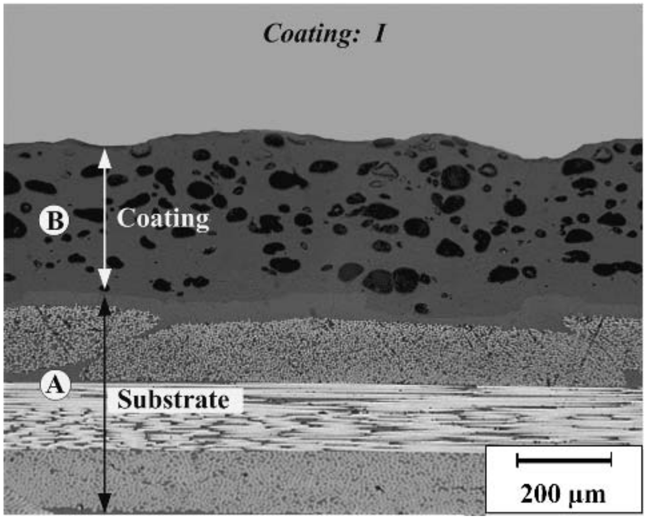

Fig. 3 Microstructure of a pure polyimide coating (B) HVOF sprayed onto a carbon-fiber reinforced PMC substrate (A)

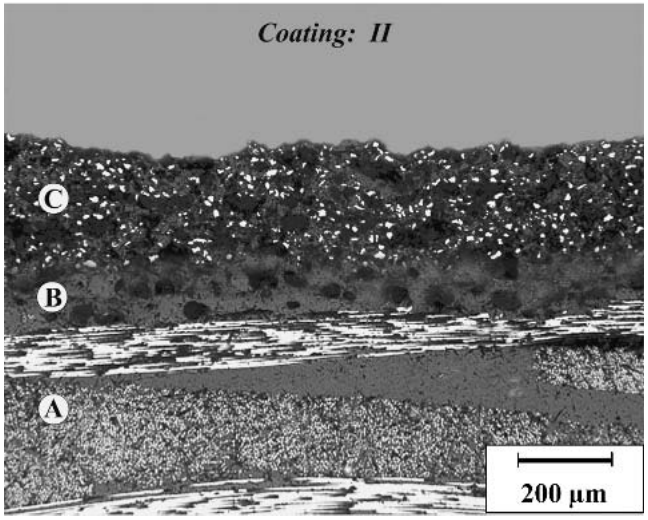

Fig. 4 Microstructure of a two-layer HVOF sprayed FGM coating composed of a WC-Co/polyimide outer layer (C) and a pure polyimide layer (B) on a PMC substrate (A)

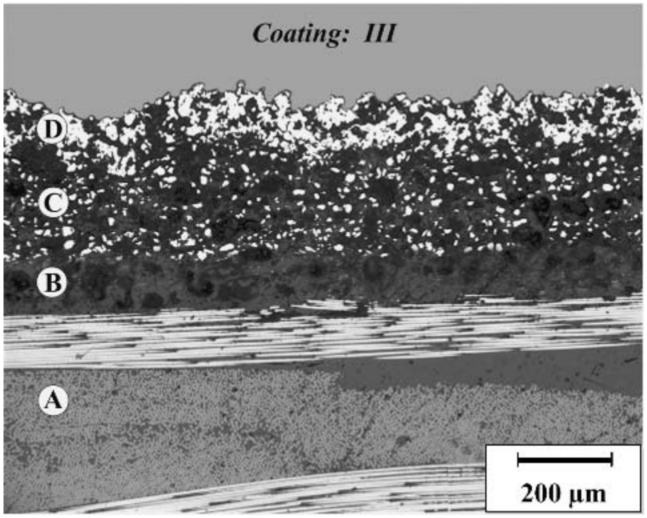

Fig. 5 Microstructure of a three-layer FGM coating comprising a pure WC-Co topcoat (D), a WC-Co/polyimide layer (C), and a pure polyimide layer (B) on a PMC substrate (A)

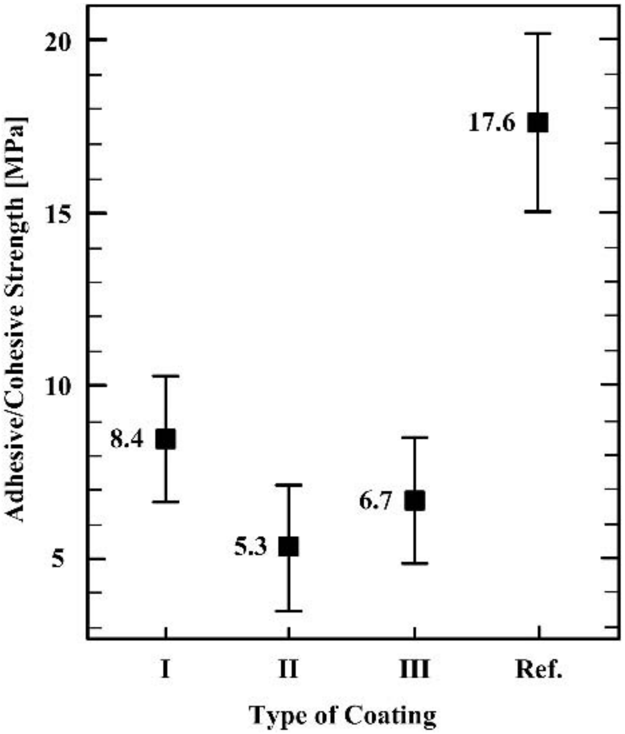

Fig. 6 Results of the tensile adhesion tests for three types of coating (I, II, and III) and uncoated reference PMC substrate (ANOVA plot)

Results of the tensile adhesion tests are shown in Fig. 6. All three coating systems exhibited adhesive bond strengths of 30 to 50% of the cohesive strength of an uncoated PMC substrate. The tensile strength of the PMC substrate was determined using the same pull-off test to establish a reference value for the substrate adhesive/cohesive properties. Uncoated substrates failed due to composite delamination in a direction perpendicular to the thickness at a tensile strength ~17.6 MPa.

Coating systems II and III, similar to those shown in Fig. 4 and 5, exhibited lower adhesive bond strengths (5-6.2 MPa) than the pure polyimide coatings (~8.4 MPa). The main results of the ANOVA analysis used to evaluate statistical differences between the three coating systems were F-ratio and the significance of F-ratio, which had values of 3.97 and 0.041, respectively. By conventional criteria using a standard critical value of 0.050, this difference closely fulfilled the requirement (significance of F-ratio < 0.050) to be considered statistically significant. This statistical significance was primarily influenced by differences between the pure polyimide coatings (I), on one side, and the other two coating systems together (II and III) on the other. The relative difference between the two FGM coating systems (II and III) was considered not to be statistically significant.

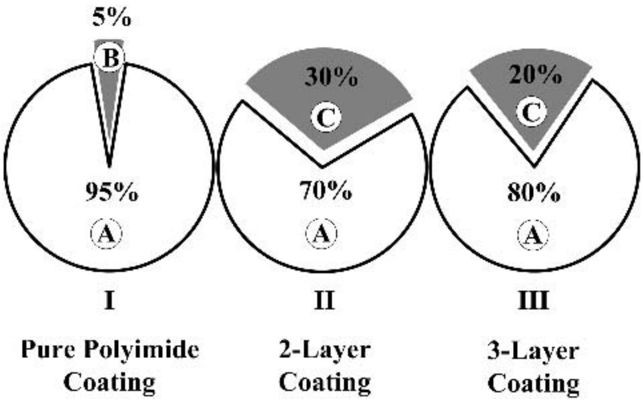

Fig. 7 Estimated percentages and locations of adhesive and cohesive failures

The locus of failure of the samples tested was characterized according to the location and percent of adhesive and cohesive failures, together with SEM characterization of the interfaces and coating layers. For the pure polyimide coating, failure occurred mainly within the PMC substrate (A) while for two- and three-layer FGM coatings, failure within both the substrate (A) and WC-Co/PMR-II layers (C) occurred, as indicated in Fig. 7.

Most of the samples thus failed due to delamination within the substrate (A). These results were surprising given that the tensile strength of the reference (uncoated) substrate (~17.6 MPa) in the direction perpendicular to thickness was much higher than the tensile strength of any of the coatings tested. This may have been due to the damage caused by the grit blasting used to roughen the substrate surfaces prior to spraying. The uncoated substrates tested were not grit blasted prior to tensile testing. Grit blasting damaged the surface of the substrate, likely reducing its tensile strength, by breaking carbon fibers at coating substrate interface, as shown in Fig. 8 (detail W).

SEM micrographs showing the failed surface of a pure polyimide coating are shown in Fig. 9 and 10. The mode of fracture in the thermosetting polyimide was brittle, associated with the formation of cracks in regions between gas voids where localized stress concentrations likely occurred. A higher magnification image of a region between gas voids (Fig. 10) showed parallel flat plateaus (also known as "river pattern"), indicating brittle crack propagation along multiple parallel planes within the polyimide coating (B).

The two- and three-layer FGM coatings both failed by the same mechanism, a combination of cohesive failure within the composite layer (region C) and cohesive failure within the substrate (region A), as shown in Fig. 7.

SEM micrographs showing the failed surfaces of tested two- and three-layer FGM coatings are shown in Fig. 11 and 12. Cracks appeared to have propagated partially along the interfaces between the WC-Co filler and the polyimide matrix, as shown on the left-hand side of Fig. 12. This may have contributed to the lower pull-off strengths measured for the two- and three-layer coatings relative to the pure polyimide coating; however, most of the tensile failures within the WC-Co/polyimide layer (region C) occurred due to crack propagation between WC-Co particles (Fig. 12).

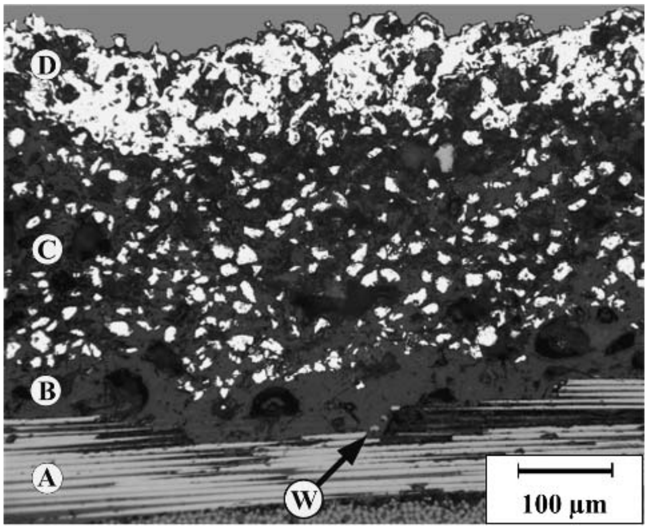

Fig. 8 Microstructure of a three-layer composite coating showing substrate surface fiber damage (W) caused by grit blasting

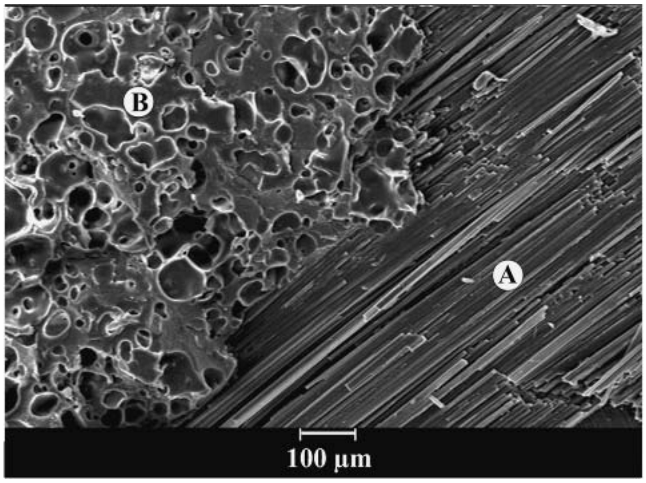

Fig. 9 Fracture surface of a failed pure polyimide coating, showing cohesive failure within the polyimide coating (B) combined with cohesive failure within the substrate (A)

5. Summary and Conclusions

The feasibility of depositing FGM coatings consisting of layers of pure thermosetting polyimide, polyimide + WC-Co, and pure WC-Co has been demonstrated using a combination of internal and external feeding of the two feedstock materials. Pure polyimide and polyimide + WC-Co were sprayed by the HVOF process and the WC-Co topcoat was flame sprayed.

The porosity and volume fraction of the WC-Co filler retained in the sprayed coatings were determined using standard metallographic techniques and image analysis. The relative proportions (on a pore-free basis) of polyimide matrix and WC-Co filler were 58 and 42%, respectively. The porosity of the pure polyimide coating was determined to be ~26%, likely due to gas evolution during cross linking of the polyimide above 280 °C.

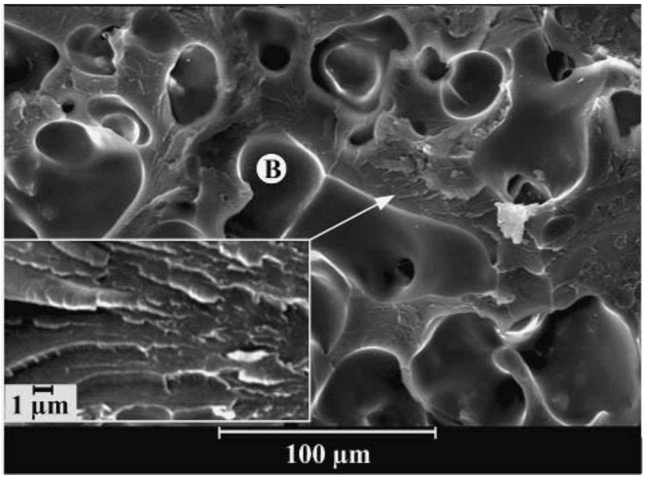

Fig. 10 Fracture surface of a pure polyimide coating (B) at a higher magnification (500×) showing details of the interpore region

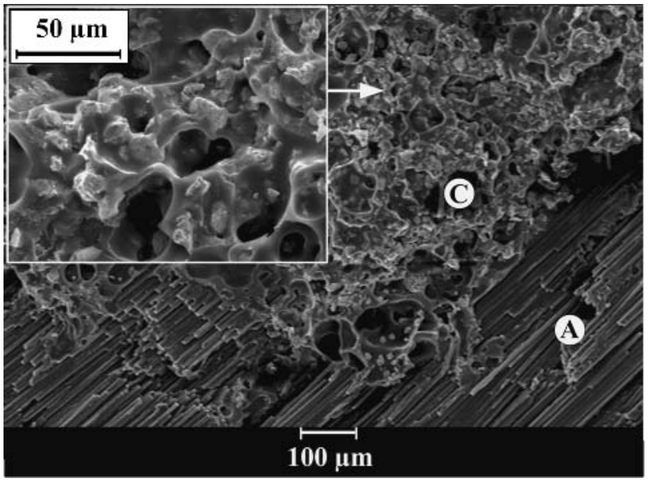

Fig. 11 Typical image of fractured surface of the two- and three-layer coating systems, showing cohesive failure within the composite layer (C), combined with delamination within the substrate (A)

The tensile adhesion behavior of three types of coatings sprayed onto carbon fiber reinforced PMC substrates has been evaluated using a standard tensile adhesion test (ASTM D 4541). The adhesive/cohesive bond strengths of the different coating types were measured and compared with that of an uncoated substrate. The two- and three-layer composite coatings both exhibited lower pull-off strengths (5-6.2 MPa) than pure polyimide coatings (~8.4 MPa), and in all cases these values were lower than the tensile strength (~17.6 MPa) of an uncoated PMC substrate used as a reference. The nature and locus of the failed surfaces following tensile testing were characterized according to the percent adhesive and cohesive failures. The majority of the failures were due to delamination within the substrate, which occurred at lower strengths than those exhibited by uncoated substrates. The difference was likely due to substrate damage caused during grit blasting prior to coating.

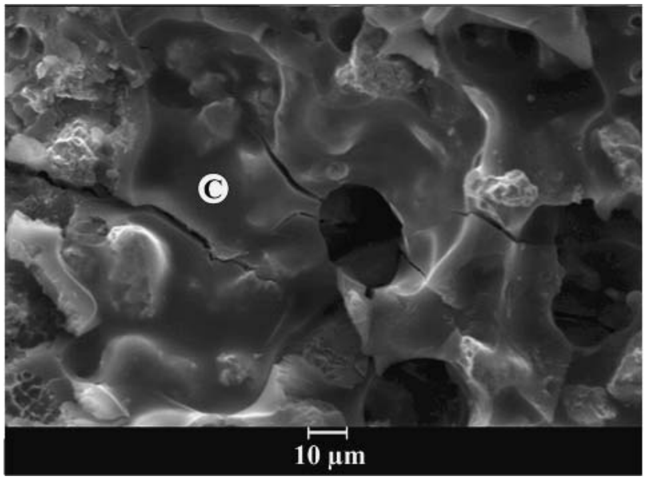

Fig. 12 Brittle cracks propagating from a pore within the composite layer (C) of a three-layer coating

The mode of failure in the thermosetting polyimide was brittle fracture associated with the formation of cracks at interpore regions where localized stress concentrations would occur. The two- and three-layer FGM coatings both failed by the same mechanism—a combination of cohesive failure within the composite layer and delamination of the substrate.

Additional work is being carried out, including continued spray parameter development and optimization, assessment of the repeatability of the results, and detailed characterization of the coatings, including evaluation of the thermomechanical fatigue properties of the coating/substrate system, and their solid particle erosion resistance. Polyimide chemistry optimization will also be investigated to reduce gas evolution during cross-linking reactions.

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