



U.S. DEPARTMENT OF  
**ENERGY**

PNNL-14246

Prepared for the U.S. Department of Energy  
Under Contract DE-AC05-76RL01830

# Final Project Report G-Plus Windshield Coatings

DW Matson  
K Koram

August 2002



**Pacific Northwest**  
NATIONAL LABORATORY

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UNITED STATES DEPARTMENT OF ENERGY

*under Contract DE-AC05-76RL01830*

Printed in the United States of America

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(9/2003)

# **Final Project Report**

## **G-Plus Windshield Coatings**

Dean Matson (PNNL)  
Kuaku Koram (PPG)

August 2002

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Pacific Northwest National Laboratory  
Richland, Washington 99352

## **Background**

Sungate® windshield coatings produced by PPG reduce solar heat loading, and hence, peak soak temperatures, in vehicles through reflection of the incident solar radiation. Reduction of peak soak temperatures could enable reduction in air conditioner power while maintaining or enhancing passenger comfort. This, in turn, would lead to a reduction in fuel usage and vehicle emission. When applied to many vehicles, the impact of this small reduction in fuel usage could be very significant. It is for this reason that reflective glazings are becoming increasingly popular in vehicles, especially in Europe. Glazing companies are involved in development programs to add value to such glazings through additional functionality such as heating for defrosting and deicing.

Sungate coatings consist of a multi-layer metal/dielectric thin film stacks capped with a thin (20 to 50 Å) protective titanium oxide layer. The dielectric layer consists of 20 to 40 nm of zinc/tin oxide and the metallic layers are 8 to 15 nm of silver with a thin (~15 Å) titanium overlayer to protect the silver from oxidation during the dielectric deposition. Sungate coatings are applied by sputtering to windshield glass surfaces and ultimately end up on the inside of a laminated glass/PVB/glass windshield. For heating functionality, copper busbars are added to the top and bottom of the laminated windshield between the PVB and Sungate coating during the lamination process to allow resistive heating for deicing applications. PPG has noted an unacceptable incidence of contact failure between the copper busbar and the Sungate coating during initial power-up. The purpose of this project was to determine the nature of the contact failure and, if possible, to ascertain the contact mechanism between the copper busbar and the Sungate coating.

PPG provided a series of samples for comparison and analysis of the copper/coating interface. These samples included:

- a “failed” section of laminated Sungate-coated windshield material,
- a section of “good” laminated Sungate-coated windshield material,
- a section of windshield glass with Sungate coating applied to one side (unlaminated, with taped edges),
- a piece of copper busbar material with adhesive and paper backing on one side and bare copper on the other side (unlaminated),
- a piece of copper busbar material with adhesive and paper backing on one side and protective release paper on the other side (unlaminated).

Instrumental analyses were performed on various samples using state-of-the-art instrumentation available in PNNL’s Environmental and Molecular Sciences Laboratory. These analyses were performed to ascertain surface and subsurface elemental composition and distribution, as well as optical and electron microscopic images.

Analytical methods applied to some or all of the samples included:

- scanning electron microscopy (SEM),
- transmission electron microscopy (TEM),
- optical microscopy
- x-ray photoelectron spectroscopy (XPS) with sputter depth profile capability.

## Sample Analysis

### Sample form and visual observations

“Failed” sample of laminated Sungate-coated windshield material:

The sample provided was approximately 6 1/4” x 8 3/4” and was cut from a section of actual windshield. The sample exhibited a slight curvature and contained both a section of clear glass (with Sungate coating) and a section of patterned glass. The pattern consisted of a roughly 2” solid black strip at one edge of the sample, transitioning into a series of black dots. A section of the dot-patterned area did not contain the Sungate coating. The sample section appears to have come from the top center area of a windshield near the area where an interior rearview mirror would commonly be mounted. An “s”-shaped section of 5/16” wide copper busbar was included in the sample and roughly separated the patterned and unpatterned areas of glass. The busbar was black on the outside of the sample (the convex side) and copper-colored on the inside (the side on which the busbar makes contact with the Sungate coating). The copper-colored side of the busbar contained a nearly continuous pattern of very fine, closely spaced dark lines. A few areas of the busbar, mostly near the edges and two or three notable areas in the center, were devoid of the lines.

“Good” sample of laminated Sungate-coated windshield material:

This sample was a section of flat glass approximately 12” on each side. The Sungate coating appears to have been applied to all surfaces of the glass with the exception of a 1/4” strip around the outside edges. Full length strips of 1/4” copper busbar were laminated on opposing edges of the sample within the coated areas of the glass. The busbar contained no pattern of fine dark lines as observed in the “failed” sample. There did appear to be some distinction between the appearance of the center of the busbar material and its outer edges, perhaps due to differences in contact during the lamination and bonding process. The busbar material appeared to be somewhat wrinkled near the outer edges, and wrinkles were observed to extend across the width of the busbar in a couple of areas.

Unlaminated Suncoat-coated glass sample

A 4” square section of unlaminated Sungate-coated glass was also provided for comparison with the laminated samples. Plastic tape was applied to the perimeter of the sample for protection from sharp edges. The sample was wrapped in bubble wrap, but the coated surface was otherwise unprotected.

### Sample Preparation and XPS Analysis of Sungate Coating and Laminates

Samples of the laminated glass were prepared by sectioning areas containing the copper busbar with a diamond cut-off wheel. Cuts were made within the edges of the busbar so that when the cuts were completed, the two halves of the laminated glass could be separated. One half of the separated sample contained the copper busbar and the other contained the Sungate coating that had been in contact with the copper. Care was taken to minimize coolant water ingress during the cutting process. Surfaces that appeared to have possibly been exposed to the cooling water were avoided during analysis. Two

spots of each copper and coating sample were analyzed for surface (top 20 to 50 Å) elemental composition using XPS. Analyses were also performed on the Sungate-coated surface of the unlaminated glass reference coating, both in the exposed central area of the glass and on a protected spot under the tape around the edge. The results of these analyses are presented in Table 1.

*Table 1. XPS surface elemental analyses of copper busbar and Sungate coatings from laminated (good and failed) samples, and from an unlaminated glass reference sample. The top row indicates the element and transition monitored. The numbers in-line with the sample descriptions correspond to percentages of a given element detected in the sample.*

sample description	C1s	N1s	O1s	Na1s	Si2p	P2p	Ca2p	Cr2p3	Ti2p	Cu2p3	Zn2p3	Ag3d	Sn3d5	Bi4f
Cu strip (good, lam.) area 1	51.3	2.7	34.0	0.4	2.3	2.0	2.6	0.7		4.0				
Cu strip (good, lam.) area 2	48.7	3.3	34.9	0.1	2.7	3.6	3.4	0.7		2.7				
Cu strip (failed, lam.) area 1	77.5	0.9	18.1				0.5			0.7	1.7	0.1	0.6	
Cu strip (failed, lam.) area 2	76.4	0.8	19.2				0.6			0.8	2.1		0.2	
coating (unlam.) under tape	36.8	0.4	41.9		17.4				2.5		0.7		0.3	
coating (unlam.) exposed	63.9	1.5	26.8		3.5				2.7		1.0		0.6	
coating (good, lam.) area 1	43.6	3.2	39.8	1.0	2.2		0.3		7.1	1.0	1.9			
coating (good, lam.) area 2	45.7	3.3	37.7	0.9	2.2		0.2		7.1	1.0	1.9			
coating (failed, lam.) area 1	59.4	0.6	29.5				0.4		3.9	1.1	3.0		0.8	1.3
coating (failed, lam.) area 2	56.3	0.6	31.9				0.4		3.8	1.0	3.5		1.3	1.2

The results shown in Table 1 indicate high carbon concentrations on all samples analyzed, suggestive of contamination resulting from atmospheric exposure and handling. Since the carbon concentrations vary significantly from sample to sample, and because the sum of all elements detected is normalized to 100%, quantitative comparisons of other elements between samples is probably not fully valid. However, a qualitative comparison may provide some insights. For example, when comparing the elements present on the surfaces of the copper busbars from the “good” and “failed” samples, there are distinct differences in the concentrations and/or the presence or absence of certain elements. Some of these differences may reflect minor compositional differences in the busbar material itself, since the width of the material was different in the two samples and it may have come from a different source. More likely, however, since the copper signal was very low for analysis of both samples, the other elements detected were contaminants from another source. One telling observation was the presence of zinc and tin on the surface of the busbar material from the failed sample, presumably appearing a result of transfer of these materials from the Sungate coating during the event causing contact failure. Zinc (but not tin) also appeared on the surface of the laminated/good coating sample, perhaps suggesting some migration of this component during operation. Interestingly, titanium was not detected on the surface of either busbar sample, despite the fact that the contact surface for the busbar is a titanium dioxide layer.

XPS analyses of the Sungate coatings on good/laminated, failed/laminated, and unlaminated samples also provided some interesting, although probably not definitive, results. A high silicon signal (and correspondingly low carbon signal) on the

unlaminated coated sample that had been covered by tape probably can be attributed to the tape adhesive. A copper signal was detected on the samples that had been laminated and in contact with a copper busbar, indicating some transfer of the copper from the busbar to the coating surface. No copper was detected on the unlaminated coating sample. There appeared to be significant variations in the titanium, zinc, and tin detected in the three samples. This may, in part, reflect variations in the thickness of the TiO<sub>2</sub> capping layer on the Sungate coating, which in turn could affect the current transfer across this layer on power-up. The appearance of bismuth on the surface of the Sungate coating in the failed laminated sample was unexpected and unexplained since that element is not used in the coating, nor was it detected in unused busbar material (see below).

#### XPS analysis of busbar material

High carbon concentrations in the analyses of the copper busbars and Sungate coatings that had been laminated together, as well as the consistently bright shiny condition of as-received busbar material prompted an investigation of the busbar material itself. We suspected that there may be an organic protective layer on the busbar material surface that could detrimentally affect its performance in a windshield application. A series of tests were run in which busbar material was subjected to various solvents and abrasive treatments, then evaluated for increased oxidation tendency. Treated samples were exposed to 50°C/85% relative humidity overnight in an environmental chamber, then examined for increased oxidation. The results are presented in Table 2. Table 3 presents XPS analyses of busbar material samples treated using various solvent and abrasive treatments, as well as UV/ozone exposure in a commercially available UV/ozone treatment unit.

*Table 2. Effect of solvent and abrasive treatments on the oxidation of copper busbar material.*

<b>Busbar material surface treatment</b>	<b>Results (overnight at 50°C/85% RH)</b>
isopropyl alcohol wipe	no effect
methylbutylketone wipe	no effect
acetone wipe	no effect
xylene wipe	no effect
DeSolve photoresist stripper wipe	no effect
5 minute UV/ozone treatment	no effect
15 minute UV/ozone treatment	no effect
3 N nitric acid wipe	strong oxidation
1 N nitric acid wipe w/DI water rinse	moderate oxidation
ScotchBrite abrasive rub	mild oxidation
silicon carbide paper rub (660 grit)	moderate oxidation

Table 3. Effect of various surface treatments on the surface composition of copper busbar material.

Busbar material surface treatment	Surface Atomic Concentration (%)			
	C1s	O1s	Cu2p3	Zn2p3
no treatment	82.60	14.78	0.07	2.56
isopropyl alcohol wipe	66.90	28.13	0.92	4.05
hexane wipe	68.00	26.82	0.86	4.32
acetone wipe	68.85	26.46	0.81	3.89
5 minute UV/ozone treatment	52.35	39.40	1.40	6.86
15 minute UV/ozone treatment	31.42	53.65	2.37	12.56
1 N nitric acid wipe w/DI water rinse	81.05	14.86	4.09	0.00
ScotchBrite abrasive rub	70.06	16.41	12.57	0.95
600 grit silicon carbide paper rub	35.3	21.0	43.7	0.00

Both the oxidation study and XPS analysis indicated that common organic solvents had little effect on the carbon content on the copper surface. XPS analysis suggested a roughly 15% reduction in surface carbon concentration with application of the organic solvents compared to untreated busbar material, but this is likely as a result of removing weakly adhered environmental carbon from the copper surface. A slight increase in copper signal was also noted as a result of the solvent wipe. Application of a UV/ozone treatment, a common method of organic contaminant removal in the electronics industry, appears to reduce carbon concentration on the copper surface, and the effect apparently increases with increasing exposure time. Both the solvent wipe and UV/ozone treatment cause an increase in surface oxygen concentration that is roughly inversely proportional to the decrease in surface carbon. This was particularly pronounced for the UV/ozone treatment, where the surface oxygen content rose dramatically with increasing exposure time (from 15% in an untreated sample to 54% for a 15 minute exposure). Application of a nitric acid wipe did not appear to significantly reduce the surface carbon concentration detected by XPS, although oxidation of the sample overnight in the environmental chamber was evident as a result of this treatment. Abrasive treatment with ScotchBrite and 600 grit silicon carbide sandpaper appear to have been more successful at exposing bare copper, but achieved mixed success at reducing the surface carbon concentration. These abrasive methods did not apparently contribute strongly to oxidation of the copper surface in the time it took to transfer the samples to the XPS stage, although the longer-term oxidation test in the environmental chamber indicated that they did a reasonable job of exposing the copper to oxidation over a more extended period of time.

The presence of zinc on the surface of the busbar material was somewhat perplexing, but may make sense if a carbon-based protective coating is present on the copper material.



The zinc may promote electrical conductivity through an otherwise nonconductive coating. As the carbon content on the copper surface is reduced through a solvent wipe or through UV/ozone treatment, the apparent Zn content increases. The effect is most dramatic in the case of the UV/ozone treatment, where the carbon is removed by oxidation to volatile carbon-containing species. The metallic zinc component of a coating would not be similarly affected, so its apparent concentration would increase as the carbon component was reduced. In the case of the nitric acid treatment, a zinc component would be preferentially attacked, leaving the organic component – as also seen in the XPS results. Upon abrasive treatment, both the organic and metallic components are removed from the copper surface (Table 3). The silicon carbide paper appeared to be somewhat more effective than the ScotchBrite in removing the surface components from the copper surface. Interestingly, zinc was not detected on the surface of the busbar material that had been incorporated into laminated components (Table 1).

The accompanying XPS spectra (Figure 1) show the effect of selected solvent and abrasive treatments on the surface composition of the copper busbar material. Figure 1d shows the results of removing the surface layers of material by argon ion sputtering to expose the underlying copper material. These results confirm that the carbon and zinc components detected are surface “contaminants” and that the bulk copper material of the busbar is relatively pure.

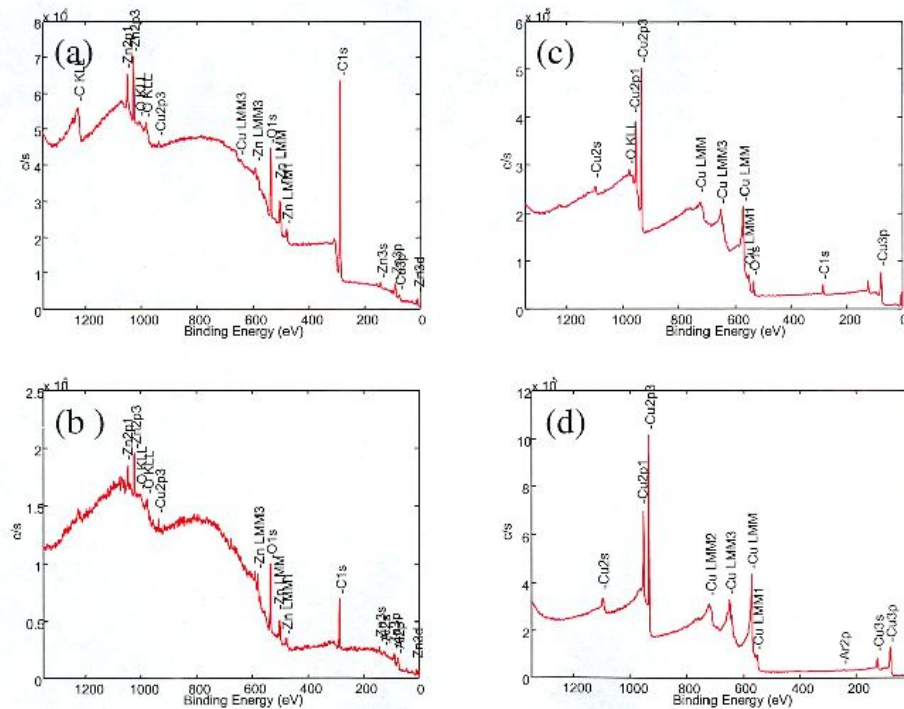
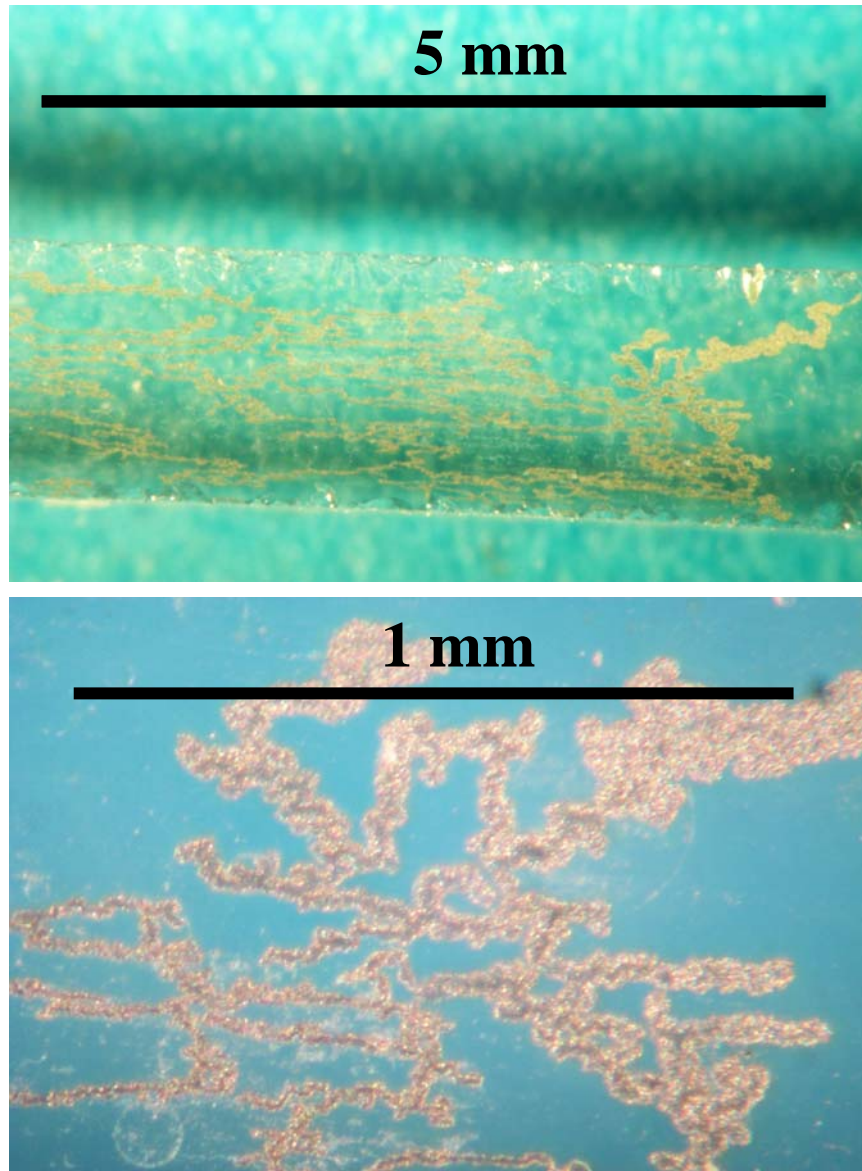


Figure 1. XPS spectra of busbar material with different surface treatments: (a) as received, (b) after ultrasonic baths in hexane, acetone, and isopropyl alcohol (15 minutes each), (c) after 600 grit silicon carbide paper rub, (d) after removal of roughly 14 nanometers of surface material by argon ion sputtering.

### Optical Microscopy, SEM, and TEM Analysis

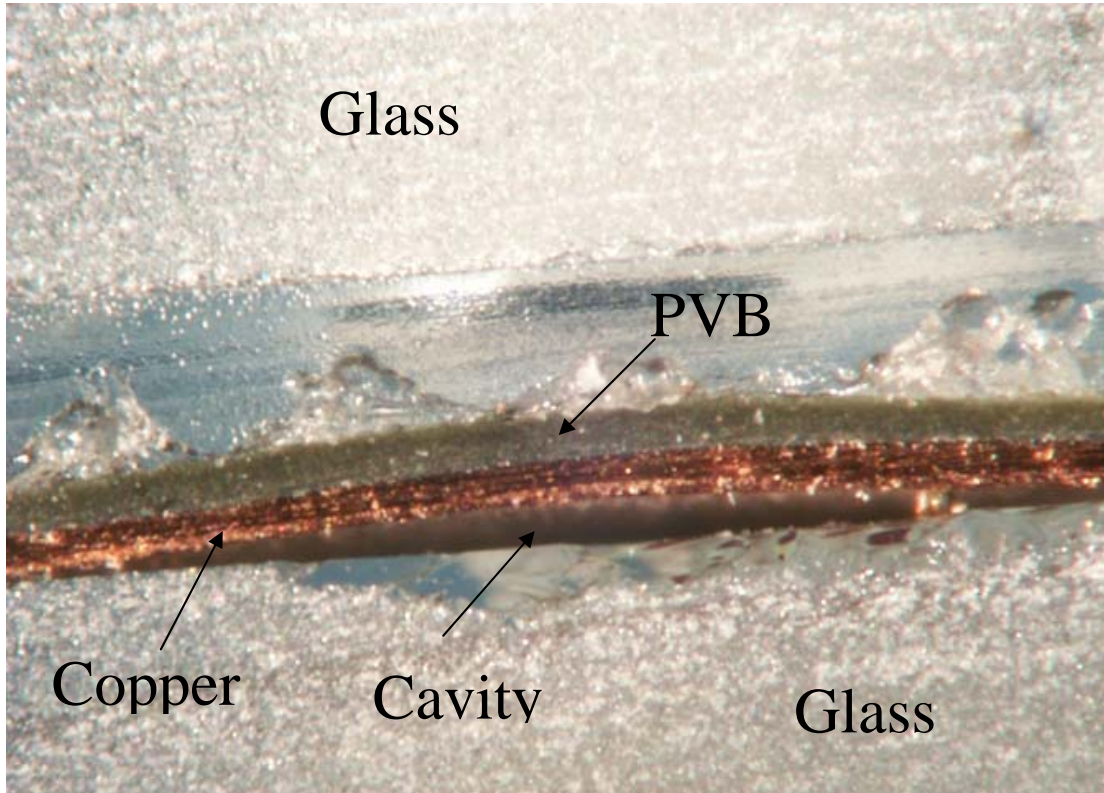
Microscopic analyses, both optical and electron, were performed on the failed laminated busbar/Sungate coating to help ascertain the failure mechanism. Optical analysis of the dark lines present between the busbar material and the Sungate coating in the failed sample of laminated windshield suggested an arc-like process was responsible for the formation of these features (Figure 2).



*Figure 2. Reflective optical micrographs of lines present at the interface between the copper busbar and the Sungate coating in a failed laminated windshield sample.*

An optical micrograph was also taken of a cross section made of an area of the failed laminated sample that did not contain the fine black lines or “tracks”. Visual inspection of the area prior to sectioning suggested that the copper may have been in poor contact with the Sungate coating at that point due, perhaps, to a slight wrinkle in the busbar

material. The cross sectional analysis confirmed that there was a gap between the copper and underlying glass in that area (Figure 3). Application of the 42V driving voltage across a small air-filled gap would provide the conditions needed to initiate a discharge ( $\sim 2.6 \times 10^6$  V/m, see Y. P. Raizer, *Gas Discharge Physics*, Springer, 1997). Such a discharge could be self-propagating since it generates localized high temperatures which, in turn, would produce more gas-phase species in the cavity.



*Figure 3. Reflective optical micrograph showing a cross section of the copper/Sungate coating interface in an area of the failed sample showing no lines such as those shown in Figure 2.*

Scanning electron microscopic analysis of the “tracks” in the Sungate coating in the failed busbar/coating interface confirmed that an arc or arc-like process produced these features. Low magnification SEM micrographs of the lines (Figure 4a) indicated that they consist of a pattern of subfeatures in a fractal-like array. A higher magnification micrograph (Figure 4b) indicates that these smaller features are a series of interconnected pits, as might be expected to be formed by a continuous arcing process. Energy dispersive x-ray elemental mapping performed on the tracked samples while in the SEM instrument (Figure 5) showed that the major elements found in the pitted areas to be silicon and oxygen. This indicates that the pitting extends completely through the Sungate coating and into the underlying windshield glass.



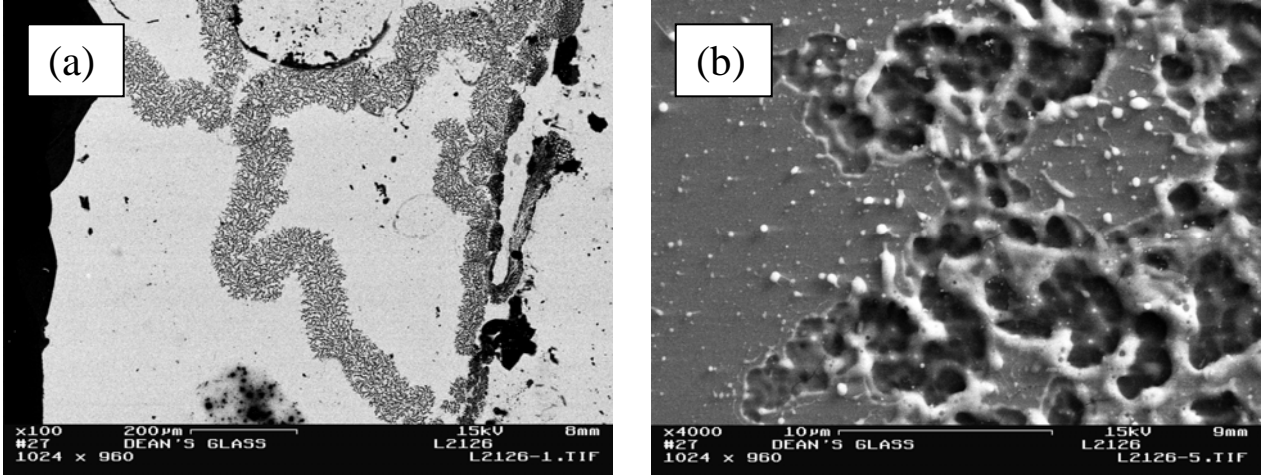


Figure 4. SEM micrographs of “track” features on Sungate coating under the busbar in a failed sample of laminated windshield at increasing magnification.

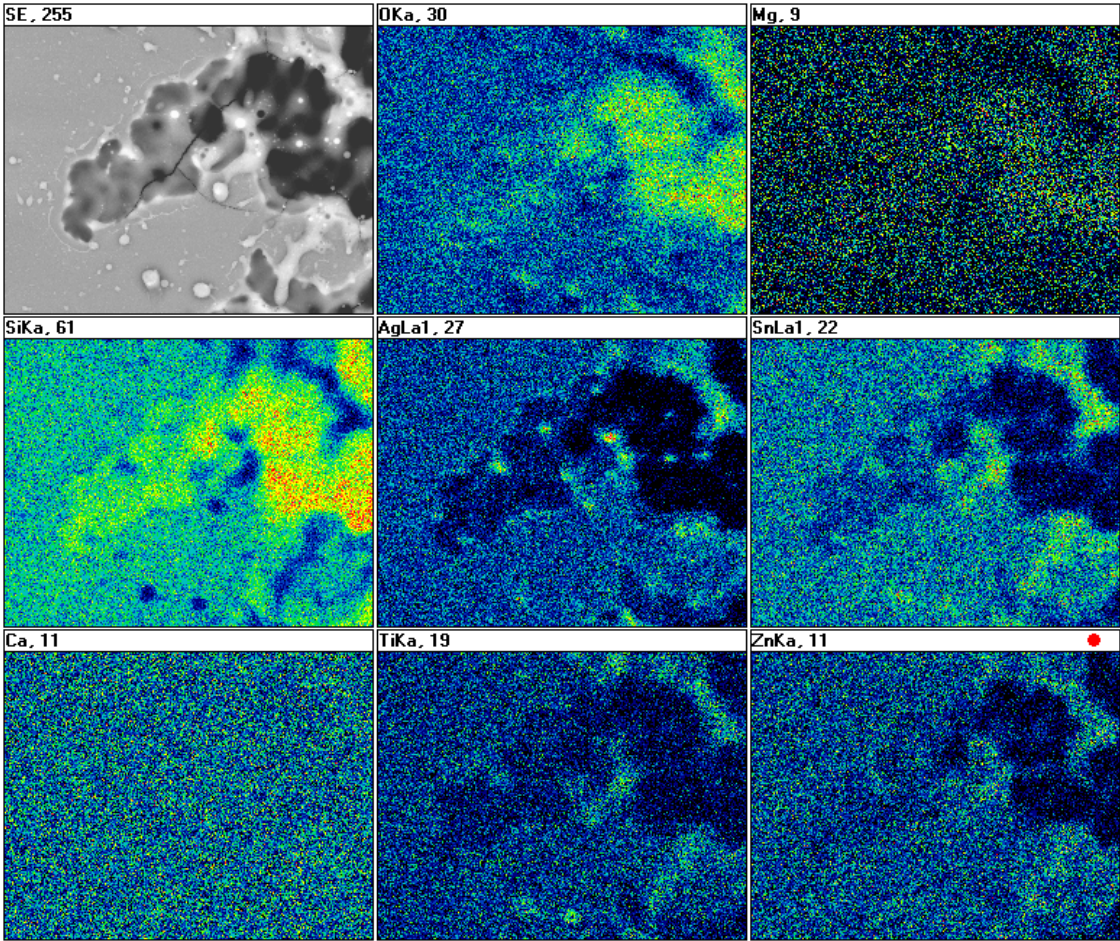


Figure 5. SEM image (top left) of pit area in damaged busbar/coating laminated sample and the corresponding EDX elemental maps for that image area.

We had hoped to be able to perform TEM analysis on the busbar/coating interface to gain insight into the current transport mechanism between the copper and the conductive layers of the Sungate coating. However, because of poor adhesion between the copper and the glass coating, it was not possible to prepare an acceptable TEM section for this purpose. Some TEM analyses were performed on cross sections of just the coating on glass from the failed laminated sample. The results of these studies suggested that the silver, which is believed to act as the conductive layer in the Sungate coating, becomes discontinuous in the areas in which arcing has occurred. This effect is seen in the attached micrograph (Figure 6), in which silver was found to be segregated into pockets. This may help account for the lack of continuity between the busbar and coating after failure.

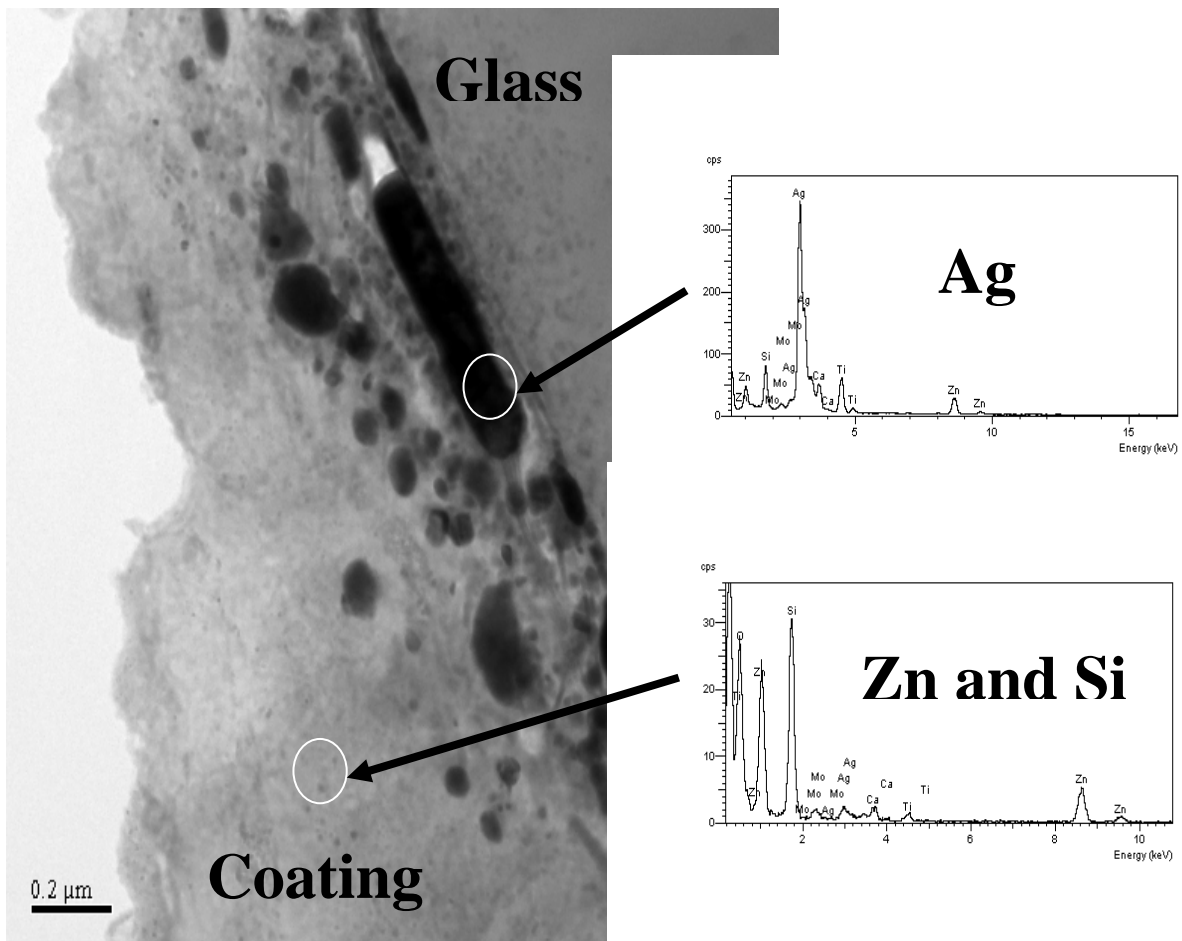


Figure 6. TEM micrograph of the glass/coating interface from failed (pitted) laminate.

## **Summary and Recommendations**

Failure of the PPG busbar/Sungate coating interface appears related to a discharge phenomenon that severely reduces the area of surface contact between the coating and busbar. The discharge is most likely initiated across an air gap incorporated into the laminate during assembly and bonding, and may be associated with wrinkles in the busbar material. The discharge appears to be self-propagating once initiated, affecting large areas of the busbar/coating interface. The presence of an apparent organic sealing layer on the surface of at least some of the copper busbar material may compound this problem through the production of gaseous organic species during the initial and subsequent discharges. This would act to maintain a relatively high pressure in the void area between the busbar and coating as the void volume grows as a result of the discharge process. The problem may be reduced by laminating the glass components under a vacuum (eliminating air in any gaps formed by irregularities in the busbar) or under an atmosphere not as conducive to discharge formation. Unfortunately, these conditions may not be easily achieved under manufacturing conditions. An alternative solution may be to reduce wrinkle formation in the busbar by automating the process of applying the busbar material to the PVB surface prior to lamination.

Although conversations with PPG staff indicated that there appeared to be no relationship between sample failure and manufacturing location, time, or material source, there did appear to be variations in the busbar material and/or Sungate coating that could affect product outcome. For example, unused busbar material provided for analysis had an apparent carbon/zinc-rich coating, whereas a zinc component did not appear on the surface of the busbar in the “good” laminated sample provided. Similarly, the presence of a bismuth component on the surface of the Sungate coating in the “failed” laminated sample appeared anomalous and may reflect coating process variations that are not apparent otherwise.

Sample preparation difficulties precluded TEM analyses that may have provided additional insights as to the contact and current-carrying mechanism between the laminated busbar/coating interface. Electrical conductivity through the zinc/tin oxide and the very thin titania surface layers almost certainly occur via an electron transport mechanism. The zinc/tin oxides are a known family of transparent conductive oxides whose resistance can vary significantly with small changes in composition. There also exists evidence, however, that some metal migration may occur, either due to thermal exposure during the glass lamination process, or due to electrical driving forces that occur on power-up. This could enhance electrical transport across the less conductive (but very thin) titania layer. XPS analysis of powered laminated samples suggested that some metallic diffusion had occurred (e.g., copper appeared the coating side and the zinc concentration increased on the coating surface).

Several further studies may help evaluate variations in Sungate coatings that could contribute to variability in coating effectiveness and/or busbar/coating failures. A systematic analysis of the Zn/Sn/O ratios in the zinc stannate layers of the coatings could yield information about sample-to-sample variations in the resistivity of this layer that, in turn, may affect coating performance. Significant variations in the chemical composition of this oxide layer could result from even minor changes in coating parameters.

Additional information about the migration of metal species could be obtained by doing depth profile analysis using Auger or SIMS on unbonded Sungate coating, a bonded but unpowered sample, and a bonded and powered sample, all from the same coating batch.