SSD-TR-92-28

②

AEROSPACE REPORT NO.
TR-0091(6935-03)-1

Space Environmental Effects on Silvered Teflon Thermal Control Surfaces

Prepared by

C. S. HEMMINGER, W. K. STUCKEY, and J. C. UHT
Mechanics and Materials Technology Center
Technology Operations

15 September 1991

Prepared for

SPACE SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Base
P. O. Box 92960
Los Angeles, CA 90009-2960

33 pgs

403965

Engineering and Technology Group

THE AEROSPACE CORPORATION
El Segundo, California

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-88-C-0089 with the Space Systems Division. P. O. Box 92960, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by R. W. Fillers, Director, Mechanics and Materials Technology Center. Capt. Don Johnson (SSD/CLPD) was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

QUANG BUI, Lt, USAF
MOIE Program Manager

Donald C Johnson Jr

DONALD C. JOHNSON JR., CAPT, USAF
Chief, STP Spaceflight Planning
Branch

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Public release is authorized;
distribution is unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
TR-0091(6935-03)-1

5. MONITORING ORGANIZATION REPORT NUMBER(S)
SSD-TR-92-28

6a. NAME OF PERFORMING ORGANIZATION
The Aerospace Corporation
Technology Operations

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Space Systems Division

6c. ADDRESS *(City, State, and ZIP Code)*
El Segundo, CA 90245-4691

7b. ADDRESS *(City, State, and ZIP Code)*
Los Angeles Air Force Base
Los Angeles, CA 90009-2960

8a. NAME OF FUNDING/SPONSORING ORGANIZATION

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F04701-88-C-0089

8c. ADDRESS *(City, State, and ZIP Code)*

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Space Environmental Effects on Silvered Teflon Thermal Control Surfaces

12. PERSONAL AUTHOR(S)
Hemminger, C. S., Stuckey, W. K., and Uht, J. C.

13a. TYPE OF REPORT

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*
1991 September 15

15. PAGE COUNT
27

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Long Duration Exposure Facility
Thermal Control Surface
Silvered Teflon
Atomic Oxygen Flux
UV Radiation Damage

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Cumulative space environmental effects on Ag/FEP were a function of exposure orientation. Samples from 19 silvered Teflon (Ag/FEP) thermal control surfaces recovered from the Long Duration Exposure Facility (LDEF) have been analyzed to determine changes in this material as a function of position on the spacecraft. Although solar absorptance and infrared emittance of measured thermal blanket specimens are relatively unchanged from control specimen values, significant changes in surface morphology, composition, and chemistry were observed.

All Ag/FEP surfaces exposed to high atomic oxygen flux (rows 7–11), irrespective of exact angle, had a uniformly cloudy appearance due to surface erosion. Scanning electron microscopy (SEM) showed a surface topography with sharp peaks and valleys, while x-ray photoelectron spectroscopy (XPS) detected a surface composition corresponding to contamination-free FEP, with less than 1 mole % oxygen.

Ag/FEP samples from rows 2 and 4, which flank the trailing edge row 3, had a nonuniform appearance, with alternating clear and cloudy bands. SEM imaging showed an intriguing variety of surface texturing in the cloudy areas, with surface

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE *(Include Area Code)*

22c. OFFICE SYMBOL

19. ABSTRACT *(Continued)*

wrinkling and puckering being most prevalent. XPS showed these surfaces to be contaminated nonuniformly with moderate to high concentrations of Si, O, C, N, and S. Ultraviolet irradiation and thermal cycling (< 0°C) are presumed to be the dominant environmental factors.

The row 1, 5 and 6 samples, which are at larger angles to the trailing edge and exposed to low atomic oxygen flux, showed little or no texture development, and no surface contamination except low oxygen (which could be due to post-flight atmospheric exposure). XPS analysis does show significant degradation of the surface FEP on these rows, which we attribute primarily to UV radiation. The surface features are consistent with FEP molecular weight degradation, branching and crosslinking through free radical reactions, which can also be induced by x-ray or high energy electron irradiation.

We hypothesize that the FEP surfaces on LDEF are degraded by UV exposure at all orientations, but that the damaged material has been removed by erosion from the blankets exposed to atomic oxygen flux and that contamination is masking the damage in some areas on the trays flanking the trailing edge.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the many contributors to this work within The Aerospace Corporation, including T. Giants, S. Gyetvay, J. Mallon, N. Marquez, and C. Su. In addition we would like to thank H. G. Pippin of Boeing Aerospace & Electronics and W. Slemp of NASA Langley Research Center for making the samples available to us, and D. Wheeler of NASA Lewis Research Center for his helpful discussions on Teflon radiation damage.

CONTENTS

FIGURES

TABLE

INTRODUCTION

Silvered Teflon (fluorinated ethylene propylene, FEP) is a light-weight thermal control material used extensively on satellite hardware. The thin silver film provides high solar reflectance while the transparent FEP Teflon overlayer gives high infrared emittance. Seventeen of the Long Duration Exposure Facility (LDEF) experiment trays were covered by Ag/FEP thermal blankets, and adhesively bonded Ag/FEP material protected a number of smaller components. Visible changes were noted on the Ag/FEP on both leading and trailing edges during the initial observations upon retrieval of LDEF. Changes included surface cloudiness, discoloration and delamination at the metal/polymer interface. The leading edge blanket surfaces have become diffuse and appear uniformly cloudy. The trailing edge blankets exhibit clear areas that are visibly unaffected, and cloudy areas. Some of the adhesively bonded Ag/FEP surfaces are significantly discolored; discoloration was also observed on many blanket edges near vents.

Solar absorptance and infrared emittance measurements on samples from the thermal blankets with 5 mil FEP have determined that material exposed to the space environment has values that are relatively unchanged from those of control specimens (Ref. 1). This includes samples with extensive visible changes such as the diffuse leading edge blanket surfaces. Material with a thinner FEP layer, e.g. adhesively bonded Ag/2-mil FEP, did show a significant change in infrared emittance due to a greater loss of the FEP layer to atomic oxygen erosion (Ref. 2). Highly discolored areas of Ag/FEP also have measurably changed thermal control properties.

In this study, samples of Ag/FEP were analyzed from as many LDEF locations as available to determine surface changes in the material as a function of position on the spacecraft. Significant changes in surface morphology, composition and chemistry were observed.

EXPERIMENTAL METHODOLOGY

SAMPLES

Ag/FEP samples for this investigation were obtained from 10 of the 12 rows of the LDEF . Exposed and protected edge samples from 14 of the 16 blankets from the A0178 High-Resolution Study of Ultra-heavy Cosmic-Ray Nuclei (Dublin Institute for Advanced Studies and European Space Agency, ESTEC) were obtained through the Materials Special Investigation Group. Many of these pieces were cut from the ground strap section. A sample from the P0004-1 Seeds in Space Experiment (George W. Park Seed Company, Inc.) blanket was provided by NASA Langley. Adhesively bonded samples were obtained on row 9 from M0003, Space Environment Effects on Spacecraft Materials, of The Aerospace Corporation and from the A0076 Cascade Variable-Conductance Heat Pipe Experiment of McDonnell Douglas Astronautics Company. A map showing the shaded areas from which samples were obtained is shown in Figure 1. A schematic representation of the blankets is shown in Figure 2, indicating the Teflon, silver, Inconel, and paint, which comprise the entire blanket structure as used on LDEF.

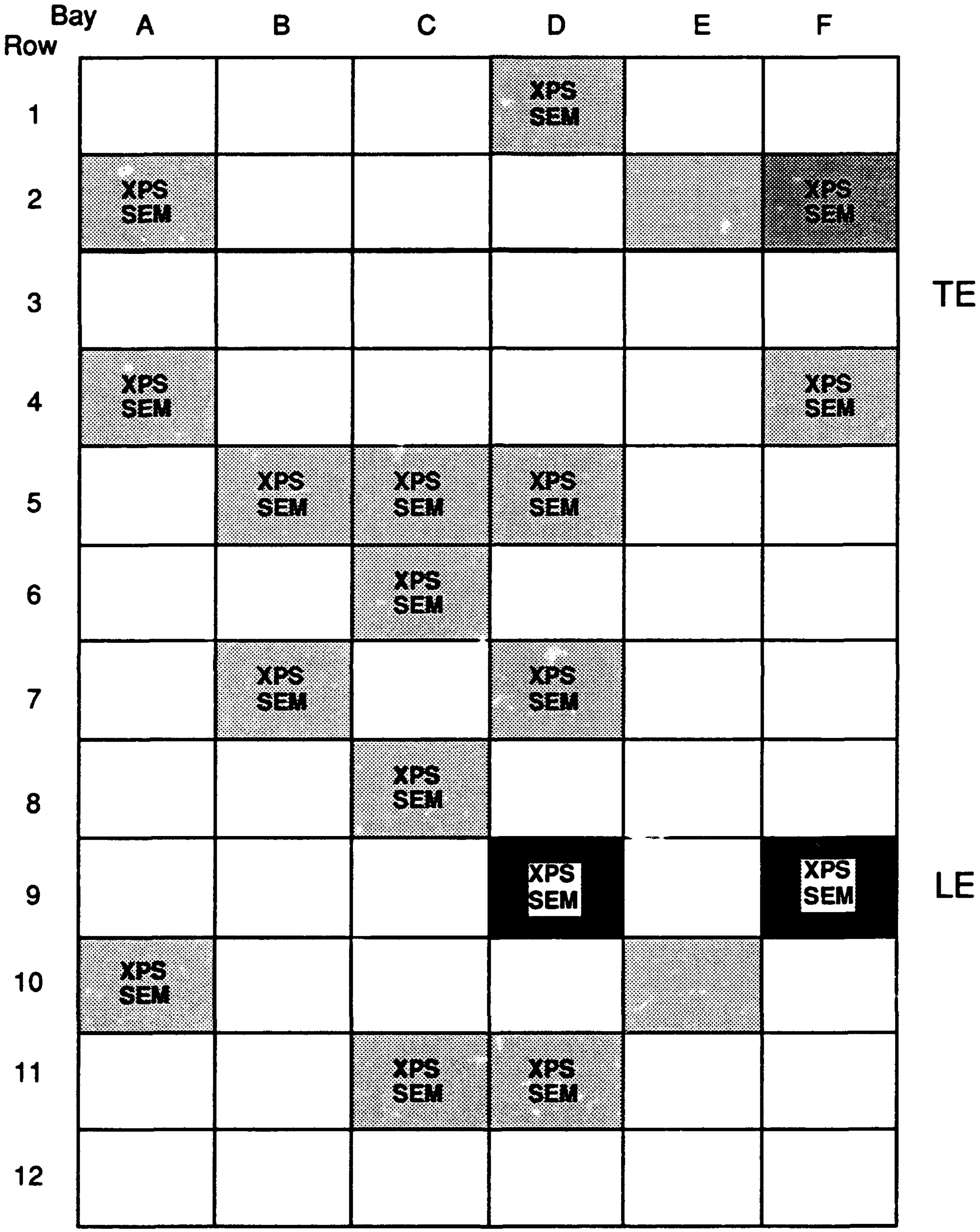
SCANNING ELECTRON MICROSCOPY/ENERGY DISPERSIVE X-RAY SPECTROSCOPY (SEM/EDS)

Ag/FEP samples from 9 of the 12 rows have been examined by SEM/EDS; their locations are indicated on the Figure 1 map. The FEP surfaces were coated by carbon evaporation to minimize surface charging effects. A JEOL 840 SEM with an EDAX 9900 EDS system was used for this study, producing electron micrographs using a 5 kV accelerating voltage.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

One or more sections of each available Ag/FEP sample was analyzed by XPS using a VG Scientific LTD. ESCALAB MK II. Samples were mounted on standard sample stubs with double-sided tape. The Mg Kα source was chosen for x-ray irradiation. Survey scans from 0 to 1100 eV binding energy were acquired to qualitatively determine the sample surface composition; analysis depth is about 50 - 100 Å. High resolution elemental scans were subsequently run to obtain semi-quantitative elemental analyses from peak area measurements and chemical state information from the details of binding energy and shape. Surface charge corrections were made by setting the F1s peak binding energy to 289.0 eV. Measured peak areas for all detected elements were corrected by elemental sensitivity factors before normalization to give surface mole %. The quantitation error on a relative basis is ≤10% for components >1 mole %. Large uncertainties in the relative elemental sensitivity factors can introduce absolute errors of a factor of 2 or even greater.

All elements of the periodic table except H and He can be detected by XPS with a Mg Kα source. The detection limit is about 0.1 surface mole %, but spectral overlaps between large peaks and small peaks can make it impossible to detect minor components.



Bay Row	A	B	C	D	E	F	
1				▨ XPS SEM			
2	▨ XPS SEM				▨	▩ XPS SEM	
3							TE
4	▨ XPS SEM					▨ XPS SEM	
5		▨ XPS SEM	▨ XPS SEM	▨ XPS SEM			
6			▨ XPS SEM				
7		▨ XPS SEM		▨ XPS SEM			
8			▨ XPS SEM				
9				■ XPS SEM		■ XPS SEM	LE
10	▨ XPS SEM				▨		
11			▨ XPS SEM	▨ XPS SEM			
12							

Figure 1. Silvered Teflon blanket locations on LDEF are indicated by shaded areas. Blankets used for SEM and XPS studies are also shown. Row 9 samples are adhesively bonded.

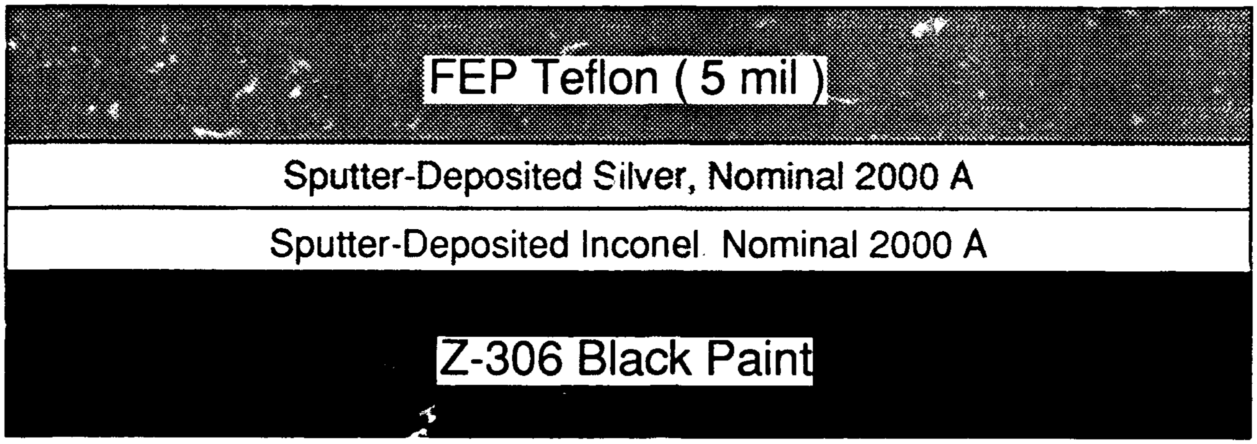


Figure 2. Schematic of 5-mil silvered Teflon thermal blankets.

RESULTS AND DISCUSSION

The leading edge samples were uniform in appearance from rows 7 through 11. Typical results of analyses with SEM and XPS are shown in Figure 3. The control surface, which is a non-flight FEP surface, is featureless in the SEM while the flight sample shows a typical erosion pattern in FEP for high velocity atomic oxygen erosion. The XPS data for the control surface shows carbon and fluorine only. The XPS analysis of the exposed surface shows that the surface composition of the FEP remaining after the erosion is indistinguishable in carbon and fluorine composition from the control, with trace amounts of some contaminants (Si, N, S, and Cl) and measurable oxygen present. This oxygen could be from the atomic oxygen interaction or from water adsorption from the atmosphere after retrieval. Water adsorption could be enhanced on the erosion-roughened surfaces, which have much higher surface area than the control surfaces. Some variations in the erosion pattern on leading edges were observed as shown in Figure 4.

Exposed trailing edge samples were found to have developed a wide variety of surface morphologies, very distinct in appearance from the featureless control surface and the atomic oxygen eroded surfaces. The blanket surface areas that appear fogged or cloudy on the trailing edge have become sufficiently diffuse to change visibly. Many of the clear, visibly unaffected areas, however, also have morphology changes, as seen in Figure 5. Within short distances on some trailing edge samples both the surface morphology and surface contamination levels were observed to change dramatically. This is shown in Figure 6. Silicon, detected as SiO_2, is one of the most significant contaminants on trailing edge Ag/FEP surfaces. It is currently not clear if any causal relationship exists between observed morphology type and surface contamination build-up. It is possible that some morphologies will have a higher probability of trapping or adsorbing outgassed or backscattered species, thereby leading to greater surface contamination buildup. Some additional morphology types observed on exposed trailing edge FEP surfaces are seen in Figures 7 and 8. Figure 7 shows a series of closely spaced bands on a section of the thermal blanket from bay A of row 2 (A2). Figure 8 shows that some trailing edge surfaces are still relatively smooth; this was most typical of samples at larger angles to the trailing edge, e.g. rows 1, 5 and 6. EDS analysis showed the bright spots to be relatively high in Si concentration.

A summary of the SEM and XPS results is shown in Table I. The leading edge samples, from row 7 to 11, all show the roughened surface typical of atomic oxygen erosion of FEP. The XPS results indicate a clean, relatively uncontaminated surface with only small increases in surface oxygen concentration. Because of low contamination and a

TABLE I. SUMMARY OF SEM AND XPS RESULTS

LDEF Row	SEM Morphology of Exposed FEP Surface	Bay	Surface Si%	Surface O%	C1s Envelope
1	Smooth; particulate contamination	D	0.2	2	Degraded FEP
2		A	0.7	6	Degraded FEP
2		F(Boeing)	2 - 8	11 - 32	Contamination
2	Puckered texture; more distinct in cloudy bands	F(NASA)	8 - 19	30 - 51	Contamination
3 (TE)					
4	Puckered and wrinkled textures in bands	F	0.2 - 7	4 - 31	Contamination
4		A	0.1	3	Degraded FEP
5	Slightly lumpy (B)	B, C, D	0.1	3 - 5	Degraded FEP
6	Some areas of puckered texture	C	<0.1	1 - 2	Degraded FEP
7	Eroded, sharp pinnacles (B)	B, D	<0.1	0.6	Clean FEP
8	Eroded, sharp pinnacles	C	<0.1	0.6	Clean FEP
9 (LE)		D, F	0.1 - 0.8	0.8	Clean FEP
10	Eroded, rounded peaks	A	0.1	0.6	Clean FEP
11	Eroded, sharp pinnacles (C)	C,D	<0.1	0.4	Clean FEP
12					
Control FEP	Smooth, featureless		<0.1	<0.1	Clean FEP

carbon 1s (C1s) XPS spectrum indistinguishable from the control material, the leading edge surfaces are characterized as clean FEP. The C1s spectrum from the D7 blanket surface is shown in Figure 9a. Curve-fitting reveals the major CF_2 peak at 292 eV and moderate CF and CF_3 peaks (approximately 10% each) at 289.5 eV and 294 eV respectively. This matches the spectrum predicted for FEP with an approximate ethylene/propylene comonomer blend of 90%/10%.

On the trailing edge of the LDEF, changes are observed both by SEM and XPS. The surfaces have lost the smooth, featureless texture of the unexposed FEP, even when the amount of contamination remains low, as indicated by silicon concentration. The trailing edge surfaces can be divided into two categories based on the XPS data. The first is characterized by low contamination levels (Si < 1%) and a C1s spectrum, as in Figure 9b, that differs significantly from that of clean FEP, but does not have a major peak at 285 eV. The second category is characterized by moderate to high levels of surface contamination

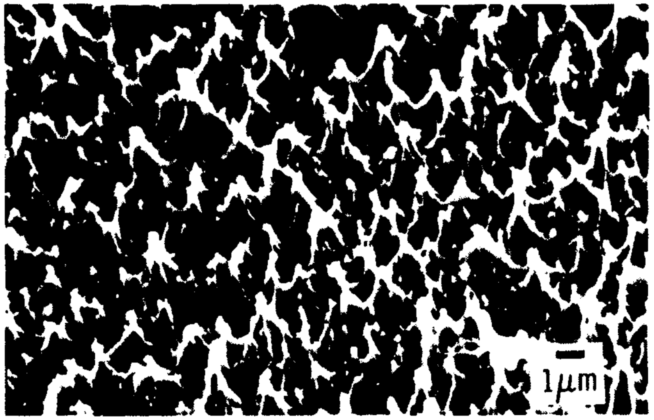
(Si, O, C, N, and S) and a C1s spectrum dominated by a peak at 285 eV, as seen in Figure 9c and d. The C1s peak at 285 eV is predominantly due to C-C bonds, and is thought to build up on the trailing edge surfaces from decomposition products of outgassed hydrocarbons and silicones.

The C1s spectrum in Figure 9b arises from degradation of the FEP surface. Curve-fitting shows that the decrease in intensity of the CF_2 peak at 292 eV is accompanied by major increases in intensity at 294 eV, 289.5 eV and 287 eV, assigned to CF_3, CF and C-$(CF_n)_4$, respectively. These changes are consistent with damage to the carbon backbone of the Teflon polymer causing molecular weight degradation, new chain terminations, branching, and crosslinking through free radical reactions. The solar ultraviolet (UV) radiation exposure of the LDEF surfaces is thought to have caused this FEP surface degradation. The FEP surfaces were also exposed to the stress of about 34,000 thermal cycles, but the maximum temperatures calculated for Ag/FEP blankets on LDEF are less than 0°C (Ref. 3) and not sufficient to break chemical bonds. Exposure of FEP to the XPS x-ray source for several hours induced similar shifts in the C1s spectrum; almost all of the FEP C1s spectra used for curve-fitting in this study were acquired during the first minute of sample exposure to the x-ray source to minimize surface degradation from the analysis itself. A recent study of the degradation of polytetrafluoroethylene (PTFE) Teflon by 3 keV electrons showed very similar XPS C1s spectra changes to those seen in Figure 9b as a function of electron irradiation and subsequent heating to drive off volatiles (Ref. 4). Degradation of the PTFE was attributed to the type of damage described above.

Future work with the LDEF Ag/FEP thermal control material at this facility will address the problem of delamination at the metal/polymer interface. This interface strength degrades during earth storage of laboratory controls, and deterioration is accelerated in the space environment. A delamination of the Ag/FEP has the potential for catastrophic failure of the material's thermal control properties; this was deterred on the LDEF blankets by the presence of the paint on the back surfaces. We are also interested in the effects of adhesive bonding on Ag/FEP performance. Discoloration and streaking was observed at the metal/polymer interface of adhesively bonded Ag/FEP on LDEF, with some degradation of thermal control properties.

Scanning Electron Microscope Image

LDEF TRAY C11 EXPOSED TEFLON



CONTROL TEFLON SURFACE

Surface Composition Determined by X-Ray Photoelectron Spectroscopy

MOLE %

C	F	O	OTHER
27	72	0.4	TRACE *Si, N, S, Cl*
27	73	TRACE	NONE DETECTED

Figure 3. Leading edge sample of Ag/FEP compared to control sample. Typical results of analyses with SEM and XPS.

AO Erosion of Exposed Leading Edge Surfaces

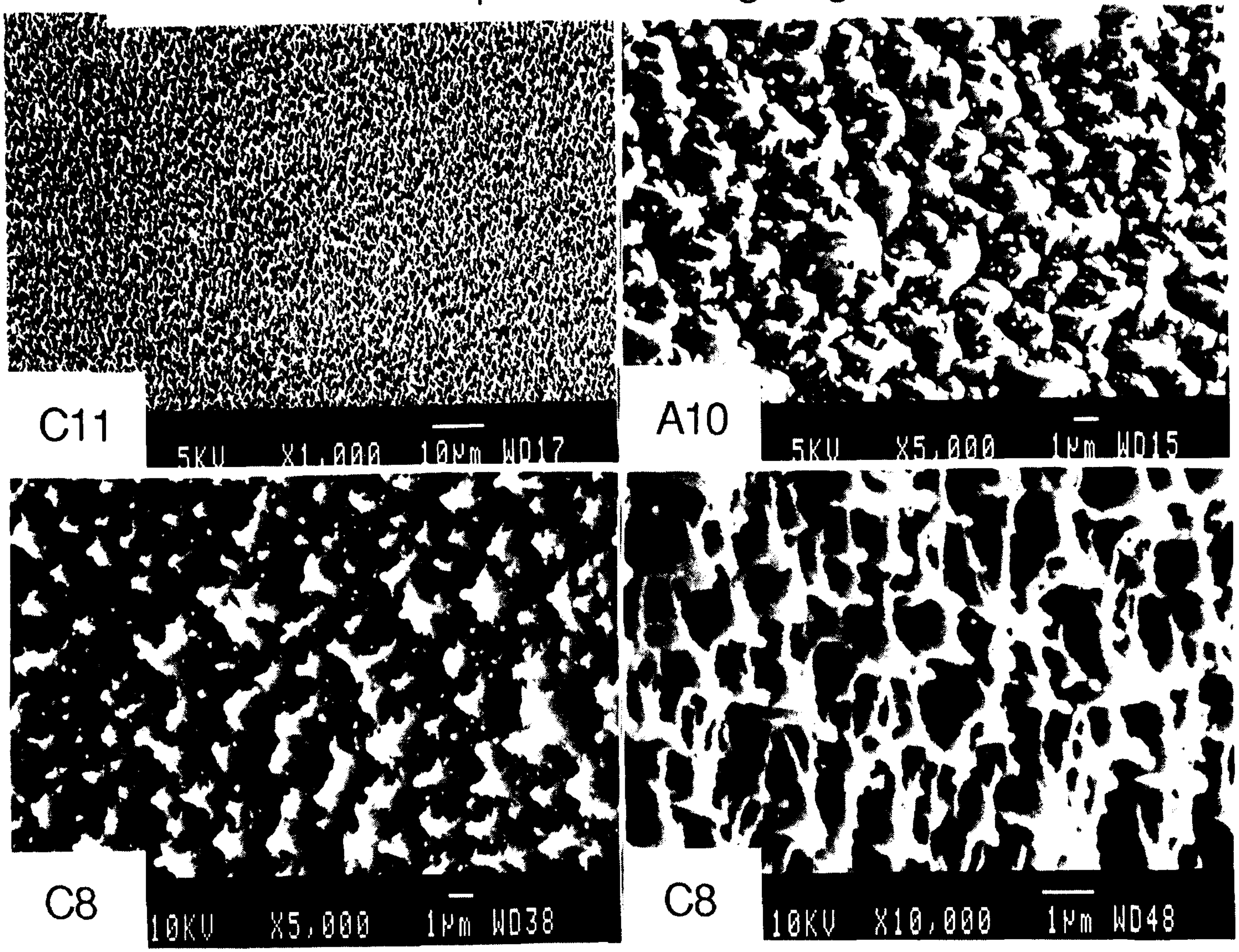


Figure 4. Some variations in the erosion pattern on leading edge samples of Ag/FEP.

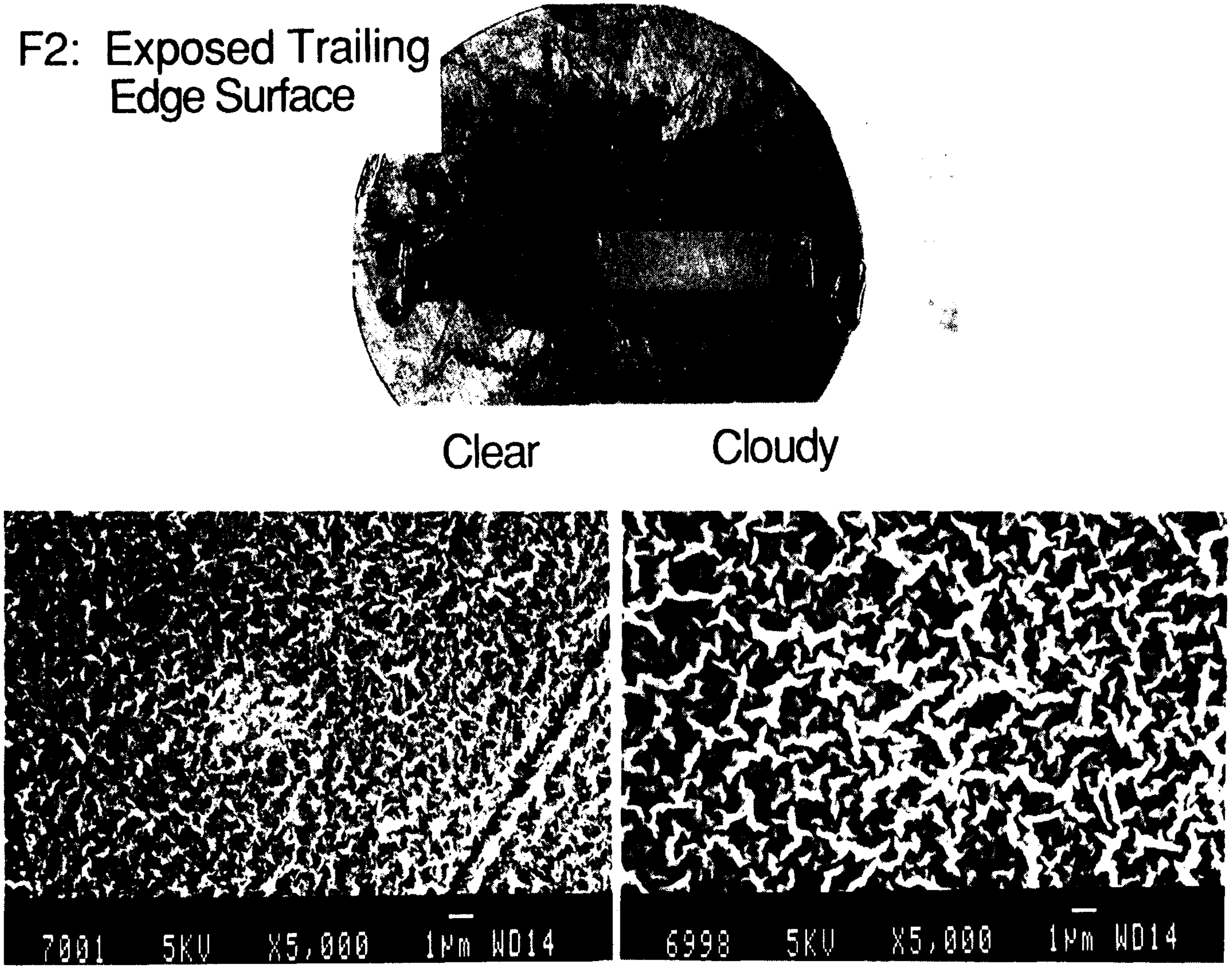


Figure 5. Exposed trailing edge surface from F2 showing morphology changes by SEM in adjacent clear and diffuse areas of Teflon.

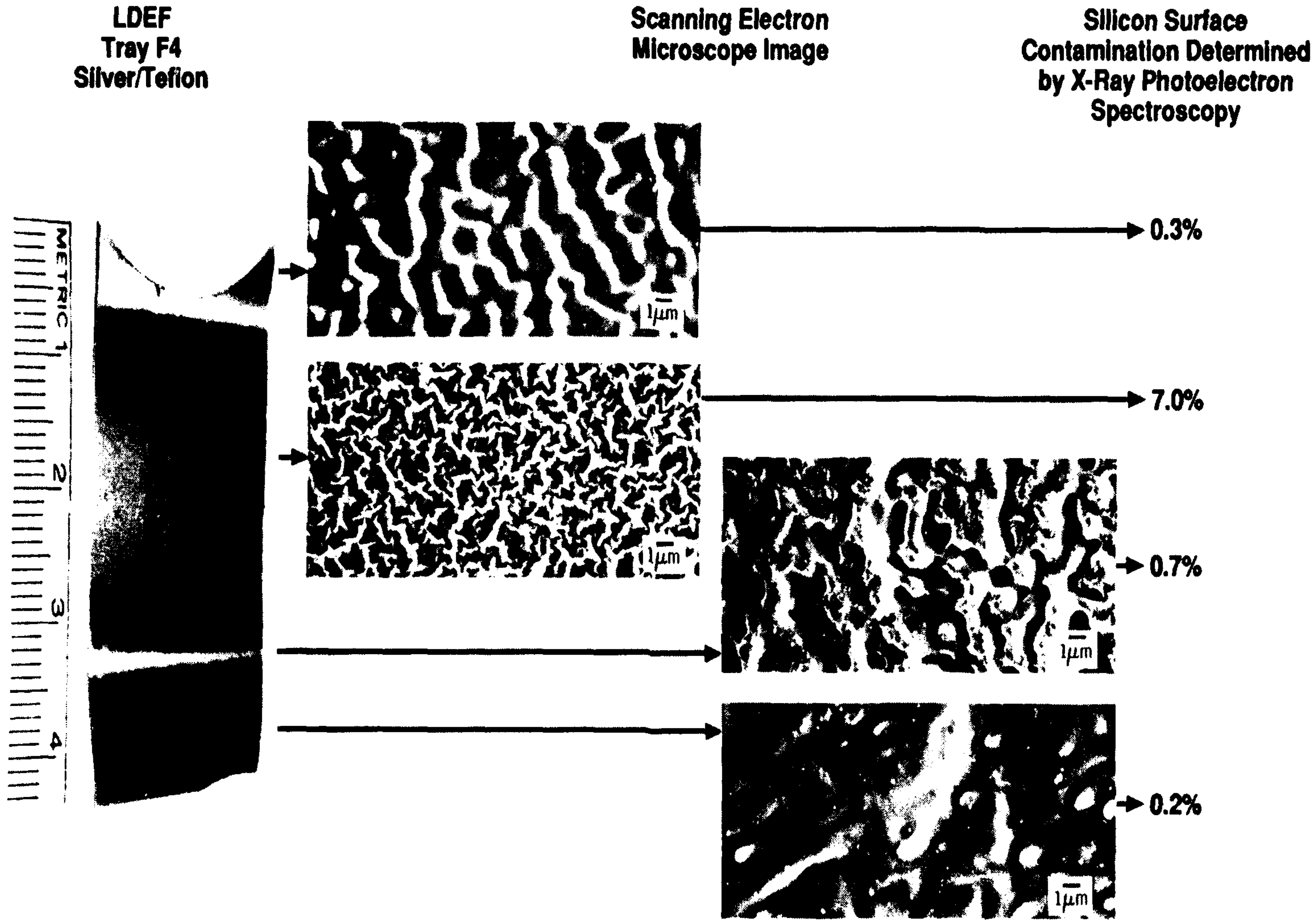


Figure 6. Changes in Teflon surface morphology and surface contamination level, as represented by Si concentration, for a series of adjacent bands on an exposed trailing edge surface from F4.

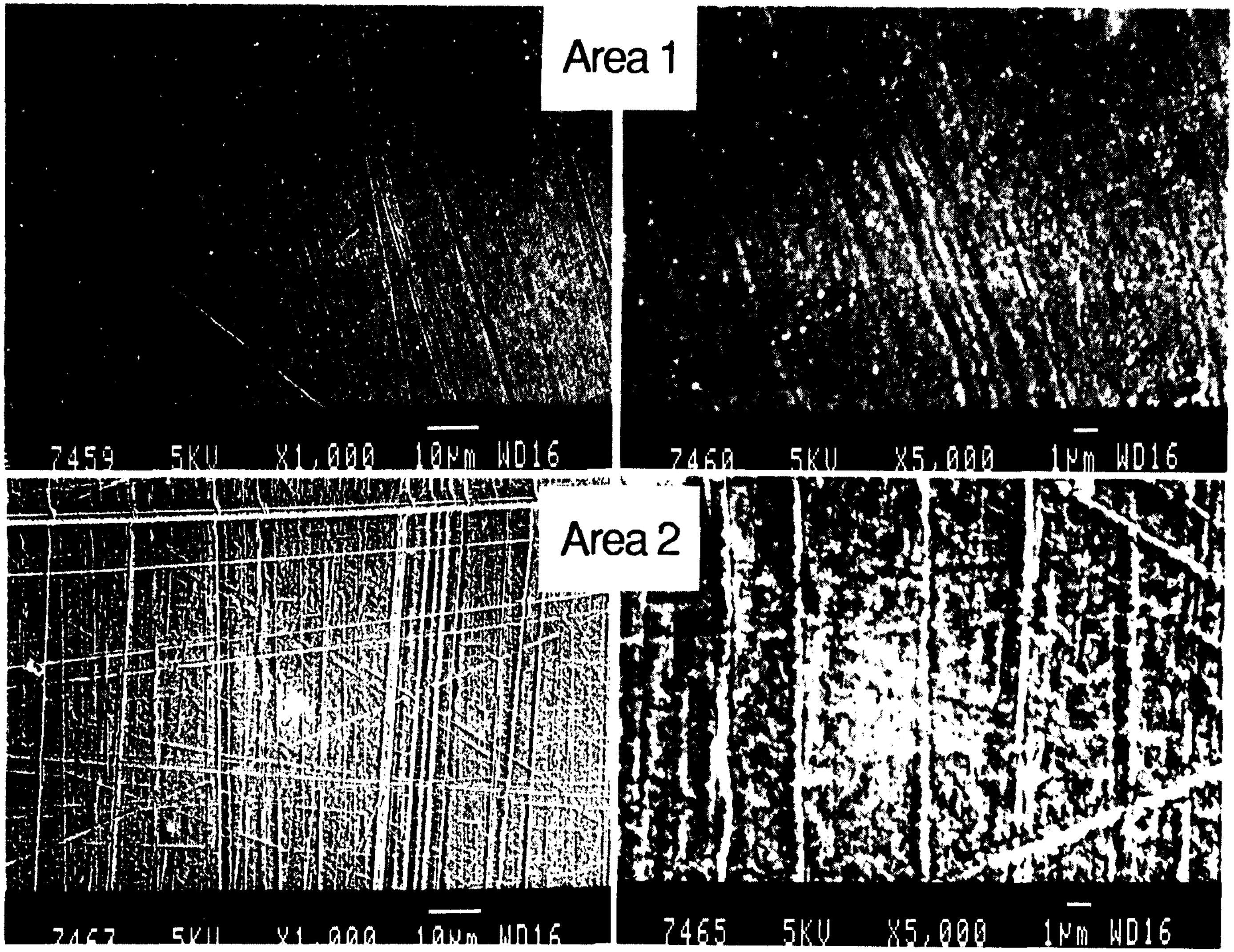


Figure 7 (Areas 1 and 2) Figure 7. SEM images of morphologies in a series of 6 closely spaced bands on a section of exposed Teflon from trailing edge A2.

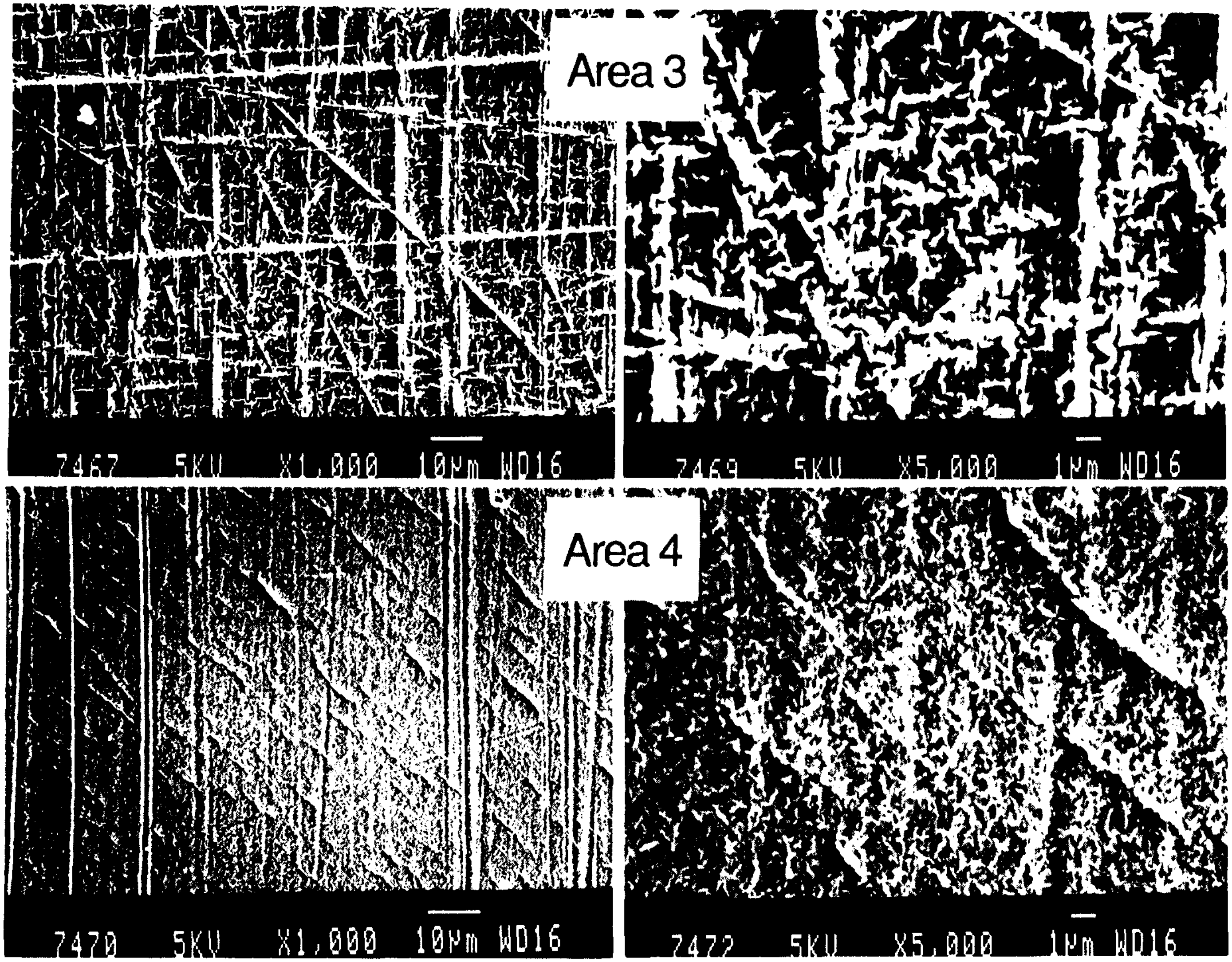


Figure 7 (Areas 3 and 4)

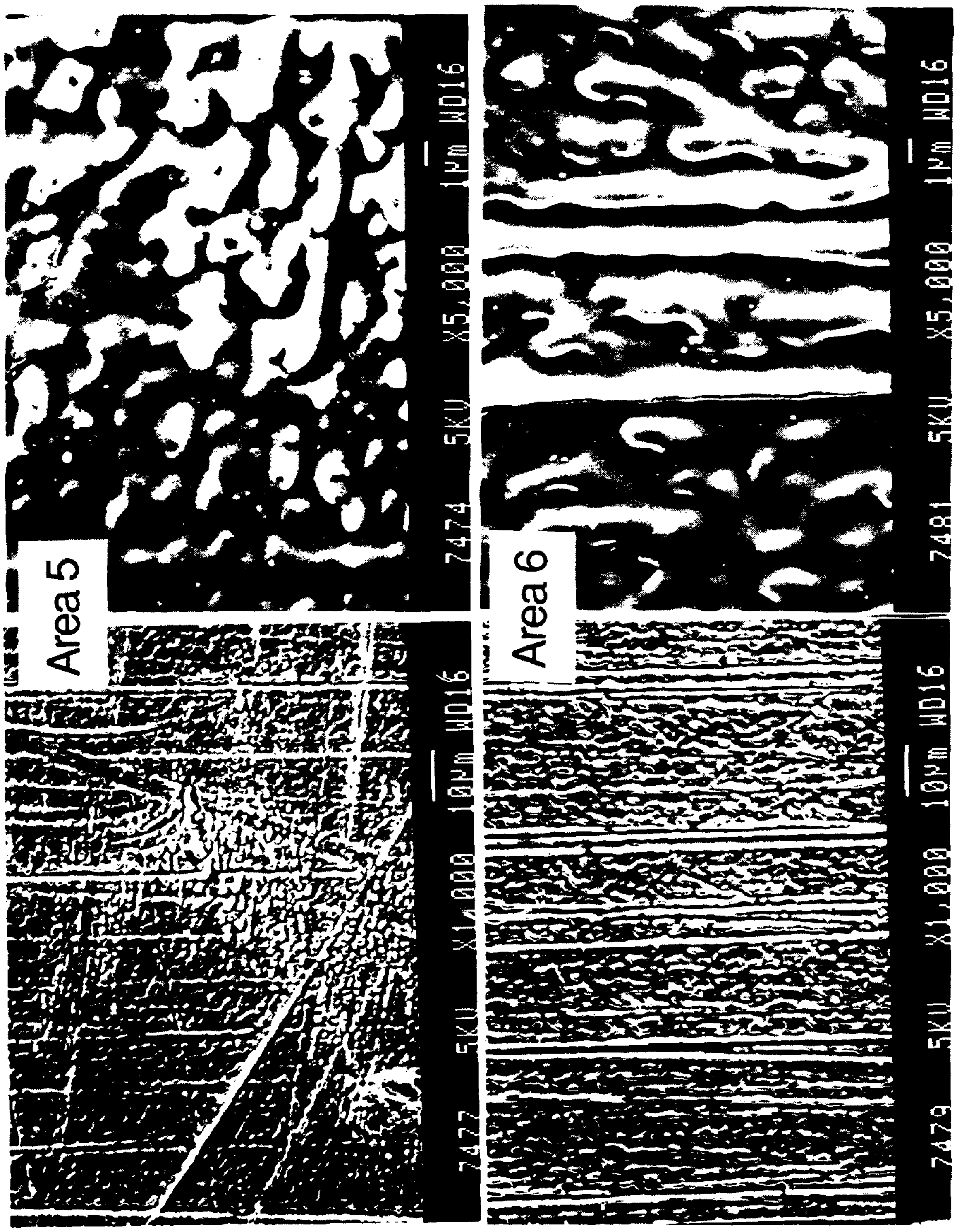


Figure 7 (Areas 5 and 6)

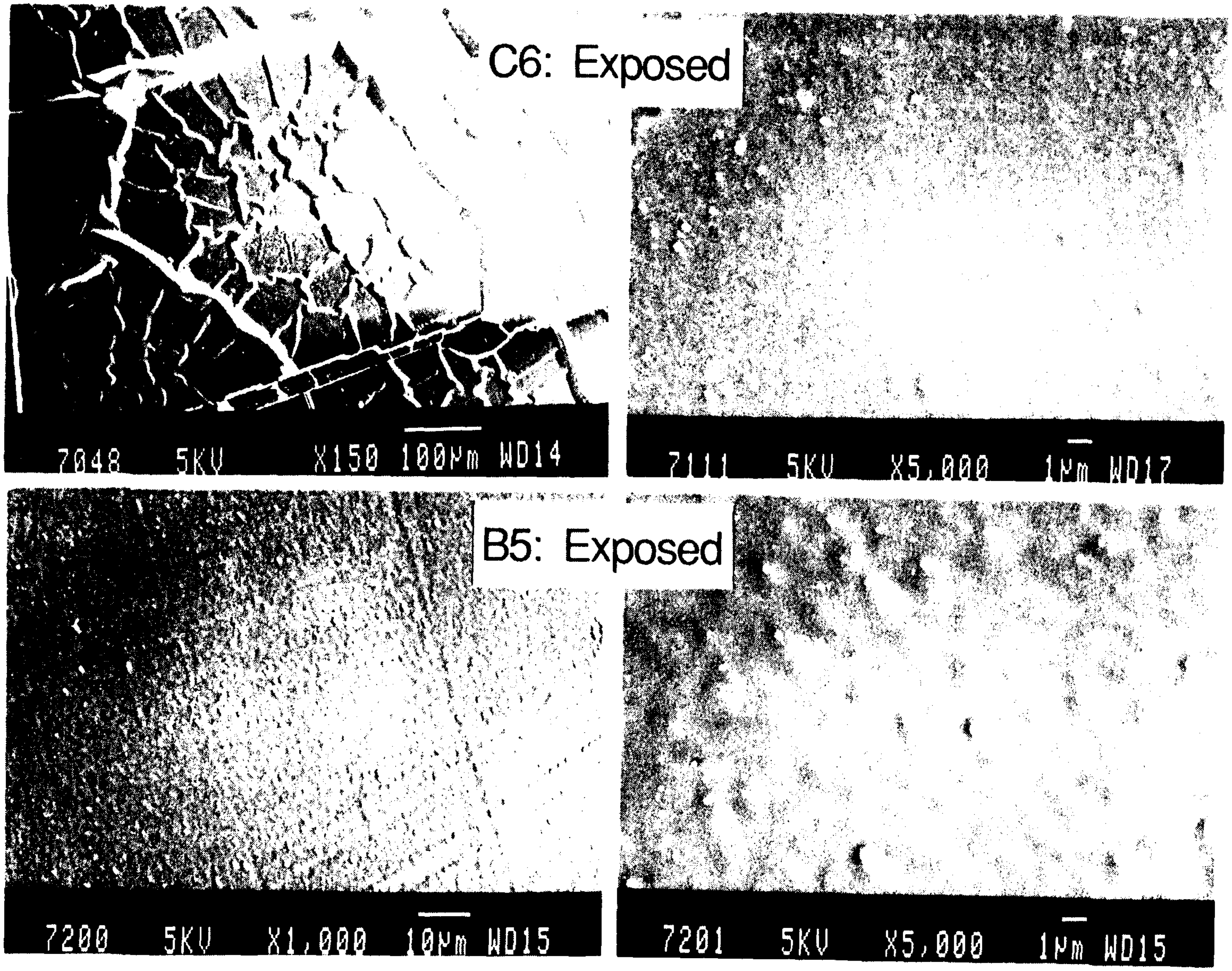


Figure 8. Exposed trailing edge surfaces that are still relatively smooth. Bright spots are relatively high in Si concentration.

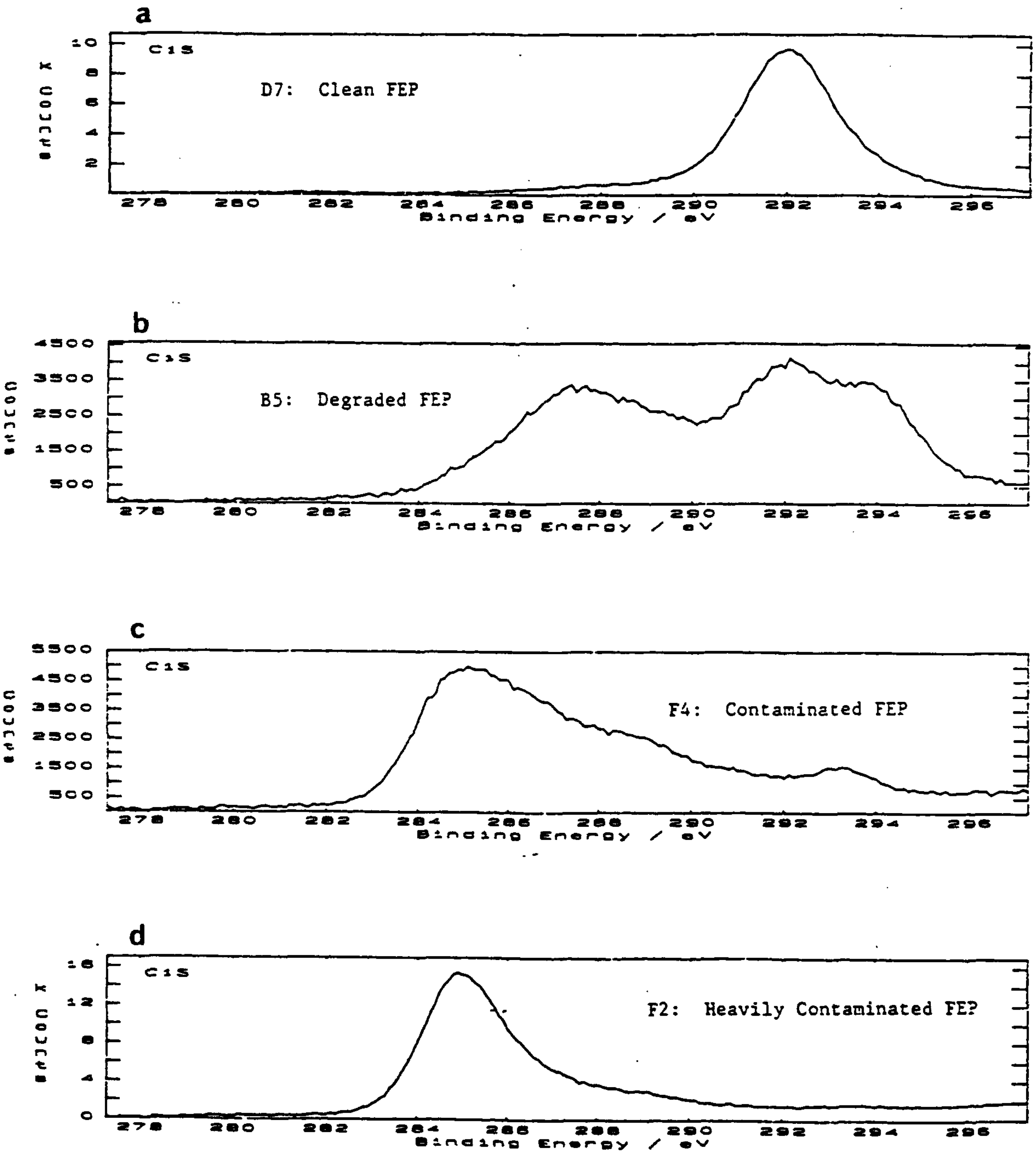


Figure 9. XPS spectra of the C1s region from Ag/FEP blanket surfaces.
a. D7 blanket surface. Characteristic of clean FEP.
b. B5 blanket surface. Characteristic of degraded FEP.
c. F4 blanket surface. Characteristic of contaminated, degraded FEP.
d. F2 blanket surface. Characteristic of heavily contaminated FEP.

SUMMARY

The cumulative space environmental effects on Ag/FEP were a function of location and exposure orientation. The leading edge of LDEF was dominated by the effect of the atomic oxygen causing erosion of the Teflon. The resulting surfaces were highly textured and not significantly contaminated; contaminants and UV-degraded FEP appear to have been removed by the surface erosion. The trailing edge samples had a wide variety of new surface morphologies in addition to the presence of more extensive contamination. On trailing edge surface areas where contamination was relatively low (particularly at larger angles to the trailing edge), XPS detected degraded FEP, most likely caused by UV exposure. This degradation appears to result from damage to the carbon backbone of the Teflon polymer causing molecular weight degradation, new chain terminations, branching, and crosslinking through free radical reactions. The UV degradation could have occurred at a slow rate during the entire mission but the erosion of the Teflon would have occurred more rapidly near the end of the mission as the altitude dropped and the atomic oxygen flux rapidly increased.

REFERENCES

1. B. A. Stein and H. G. Pippin: Preliminary Findings of the LDEF Materials Special Investigation Group. First LDEF Post-Retrieval Symposium, June 2-8, 1991. Conference Proceedings in press.

2. D. R. Wilkes, L. M. Hummer, M. J. Brown, and J. M. Zwiener: Thermal Control Surfaces Experiment (S0069) Initial Materials Investigation. First LDEF Post-Retrieval Symposium, June 2-8, 1991. Conference Proceedings in press.

3. W. M. Berrios and T. R. Sampair: LDEF Post Flight Thermal Analysis. LDEF Science Office, NASA Langley Research Center.

4. D. R. Wheeler and S. V. Pepper: X-ray Photoelectron and Mass Spectroscopic Study of Electron Irradiation and Thermal Stability of Polytetrafluoroethylene. J. Vac. Sci. Technol. vol A8, no. 6, Nov/Dec 1990, pp. 4046-4056.