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# LEVELING COATINGS FOR REDUCING THE ATOMIC OXYGEN DEFECT DENSITY IN PROTECTED GRAPHITE FIBER EPOXY COMPOSITES

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## ABSTRACT

Pinholes or other defect sites in a protective oxide coating provide pathways for atomic oxygen in low Earth orbit to reach underlying material. One concept for enhancing the lifetime of materials in low Earth orbit is to apply a leveling coating to the material prior to applying any reflective and protective coatings. Using a surface tension leveling coating concept, a low viscosity epoxy was applied to the surface of several composite coupons. A protective layer of 1000 Å of $SiO_2$ was deposited on top of the leveling coating, and the coupons were exposed to an atomic oxygen environment in a plasma asher. Pinhole populations per unit area were estimated by counting the number of undercut sites observed by scanning electron microscopy. Defect density values of 180,000 defects/cm$^2$ were reduced to about 1000 defects/cm$^2$ as a result of the applied leveling coating. These improvements occur at a mass penalty of about 2.5 mg/cm$^2$.

## INTRODUCTION

Space power components made from graphite fiber-epoxy composites and exposed to the low Earth orbital environment are subject to degradation from atomic oxygen. Atomic oxygen attacks both the epoxy and the carbon fibers forming volatile oxides. Although there are several metal oxide coatings that can be deposited on top of the epoxy, thorough coverage is difficult because dust particles, scratches, and surface irregularities create defects in the protective coating (ref. 1). These pinhole and scratch defect sites are numerous, and provide a pathway for atomic oxygen undercutting (ref. 2-3). Once started, the undercutting may progress to the extent that the protective coating tears thus allowing more epoxy to be exposed to the atomic oxygen environment.

Lightweight solar mirrors made from graphite fiber-epoxy composite face sheets are particularly susceptible to this kind of erosion. The defect sites that are inevitably in the protective coating are often too small to see, until after atomic oxygen undercutting has begun. However, based on laboratory research with samples having a large pinhole population, catastrophic optical failure of composite mirror surfaces occurs at the fluences expected at Space Station Freedom altitude over a time of 15 years (ref. 4).

One technique proposed to diminish the pinhole population in the graphite fiber-epoxy composite face sheet of a solar mirror is to apply a surface tension driven leveling coating over the composite prior to applying the reflective and protective coatings. The purpose of the leveling coating is to cover the small projections and cracks where the pinholes originate, creating a smoother surface onto which the reflective and protective coatings may be deposited, as shown in figure 1. The smoother surface finish created by the leveling coating should also enhance the specular reflectance of the mirror. A previous study using epoxies that were poured onto the substrate surface has reported an order of magnitude decrease in defect density and an order of magnitude increase in specular reflectance (ref. 1). The present study compares leveling coatings that were produced by dipping the substrates into epoxies. Subsequent improvements were found in defect density population and specular reflectance.

## MATERIALS AND METHODS

The application of a surface tension driven leveling coating was accomplished by dipping the substrate into a container of low viscosity epoxy and withdrawing the sample slowly. All samples were pulled out of the epoxy vertically. Several different epoxies were considered initially, as shown in Table I. Aluminum substrates were used for the initial screening experiments, and profilometry was used to make surface roughness comparisons between the aluminum and the epoxy-covered aluminum. The numbers to the right of each sample represent average surface roughness, in angstroms, based on the method of standard deviation by successive differences (ref. 5). Only the aluminum substrates were cured vertically. All of the other substrates were cured horizontally.

The sample with the smoothest finish after dipping was Epotek 305, manufactured by Epoxy Technology, Inc. However, the Epotek 305 had a pot life of only 20 minutes. With such a short pot life, the viscosity of the epoxy increased substantially during the course of several dipping experiments, making it difficult to produce consistent coatings.

Due to the short pot life of the Epotek 305, it was decided to continue the leveling coating work with the next best performer, Epotek 301-2, also manufactured bt Epoxy Technology, Inc. The pot life of the Epotek 301-2 was found to be much longer, allowing for several samples to be dipped (or one sample to be dipped several times) in one session. In subsequent experiments, an additive (FC-430 Flourad Brand Coating Additive, manufactured by 3M) was added to the Epotek 301-2 to enhance the wetting of the low viscosity epoxy to the T300/934 graphite fiber-epoxy composite substrates chosen for this study.

Dipping the 2.23 cm x 2.23 cm x 0.30 cm coupons was accomplished mechanically by an Oriel Miniature Motorized Translator. The dipping speed was on the order of 1 cm per minute. No time dependent studies were conducted. Each coupon was dipped half way into the Epotek 301-2 so that half of the sample was coated with a leveling coating and the other half with no leveling coating. Care was taken to mix the resin and hardener thoroughly without creating a lot of bubbles. The mixture was often allowed to settle for several minutes and a pipet was used to skim off any of the remaining bubbles from the surface. Figure 2 shows a photo of the dipping apparatus, with a sample installed.

Additional techniques for sample preparation were also considered. Some of the initial composite samples dipped in the Epotek 301-2 exhibited a tacky surface, attributed to humidity. Mixing of the epoxy, dipping, and curing were performed in a nitrogen-filled glove box to avoid the tacky surface. A simple tube furnace made from nichrome wire wound around a glass tube served as a means of curing the samples at 80°C. The temperature of the tube furnace was controlled manually, and heating was accomplished using a ramp-and-soak technique over about an hour. Samples were allowed to cure for at least another 1 1/2 hours. It was necessary to place the samples horizontally in the tube furnace during curing, which also seemed to minimize the formation of a small lip on the bottom of the composite where the epoxy would otherwise collect by gravity.

Those samples prepared for defect density counting were coated with about 1000 Å of $SiO_2$. An $SiO_2$ coating was chosen over an aluminum reflective coating because the defects generated by undercutting are best seen by charging in a scanning electron microscope and an aluminum coating would diminish the charging. Samples were coated using an electron-beam (e-beam) evaporation technique. Atomic oxygen exposure followed, using a Structure Probe, Inc., Plasma Prep II plasma asher. The asher was operated on air at 50-100 mtorr, at a continuous RF power of 100 watts. Effective atomic oxygen fluence was determined by measuring mass loss in adjacent Kapton (a product of the E. I. du Pont de Nemours & Co., Inc.) witness coupons and calculating fluence based on the erosion yield of Kapton in low Earth orbit. This was necessary because of the lack of in-space erosion yield data for the specific epoxy materials used. An erosion yield of $3x10^{-24}$ $cm^2$/atom was assumed such that the Kapton effective fluence is the epoxy effective fluence. Defect density measurements were made by obtaining several scanning electron micrographs of random leveling coated (and uncoated) regions and counting the number of defects that could be identified in the photo. Magnification was on the order of 150 to 500 times. Both secondary electron and back scattered electron images were used, but the back scattered images showed the undercutting more clearly. The area occupied by the photo was determined so that defect density could be cited as defects/$cm^2$.

Samples for reflectance measurements were prepared differently. The as-received T300/934 composite coupons were first coated with 1000 Å of aluminum, again using e-beam evaporation. Electron-beam evaporation was chosen over other deposition techniques because the reflective and protective coatings for Space Station Freedom solar dynamic concentrators were to be prepared using e-beam techniques (ref. 3). Total and diffuse reflectances were measured to an accuracy of ± 2% on a Perkin-Elmer Lambda-9 spectrophotometer equipped with a 60 mm diameter integrating sphere over the wavelength range of 250-2500 nm. Specular reflectance was determined by difference, and all three measurements were corrected to air mass zero and integrated to obtain solar integrated reflectance values. Then, the samples were dipped entirely in the Epotek 301-2, so that the whole mirror face was coated with epoxy. After curing at 80°C, 400 Å of gold were deposited via sputter deposition to inhibit curtaining (a roughening of the surface attributed to uneven heating) of the epoxy and another 1000 Å of aluminum were e-beam deposited on the surface. Total, diffuse, and specular reflectance were measured again, for comparison to the non-leveling coating values.

The reflectance samples were also subjected to atomic oxygen exposure in the plasma asher. Again, Kapton witness coupons were used to confirm the atomic oxygen fluence.

In addition to the graphite fiber-epoxy substrates used for the bulk of the study, a small fused quartz slide was used as a substrate in one part of the study to compare the atomic oxygen defect density of a leveling coating on a generically different substrate with that of the graphite fiber-epoxy substrate.

## RESULTS AND DISCUSSION

The leveling coatings described in this paper provide two benefits for low Earth orbital space systems. For satellites that will reside in low Earth orbit, the leveling coating provides a means to reduce atomic oxygen degradation by reducing the number of atomic oxygen susceptible defect sites. And for satellites using a solar mirror, the leveling coating also provides a means to increase the solar specular reflectance of a light-weight graphite fiber-epoxy substrate.

### Atomic Oxygen Durability

The degree of improvement in atomic oxygen durability was determined by comparing the defect density of the pristine graphite fiber-epoxy composite surface with the defect density of the surface after one application of the leveling coating. Figure 3a shows a scanning electron micrograph of one of the non-leveling coating surfaces coated with $SiO_2$ after ashing to a fluence of $1.75 \times 10^{21}$ atoms/cm$^2$. Figure 3b shows another scanning electron micrograph of the adjacent region coated with Epotek 301-2. Undercutting defects are best identified by the rings around each of the initial pinhole defects, produced by charging under the electron beam. Note the variety in the size and shape of the undercutting defects. The size and shape of the defects shown here are similar to the ones that have been characterized before (ref. 6). Given more time in the atomic oxygen environment, the undercut areas would grow together causing the coating to tear, making it impossible to count the number of defects sites. Having such a variety in defect size, shape, and extent, defect density counting remains somewhat inexact. However, with the selection of the proper fluence of atomic oxygen, the technique of counting defects on scanning electron micrographs can be useful for the purpose of sample comparison, at least to an order of magnitude.

Table II summarizes the non-leveling and single leveling coating data collected for both the graphite fiber-epoxy substrate samples and the fused quartz samples. Although there is some scatter in the data, the uncoated samples of graphite fiber-epoxy show a defect density on the order of $10^5$ defects/cm$^2$ while the coated samples show a defect density on the order of $10^3$ defects/cm$^2$. Hence, for these graphite fiber-epoxy samples, the leveling coating provides a two order of magnitude improvement in the atomic oxygen defect density. Although there are no data for the fused quartz slide before dipping, the fused quartz slide with a leveling coating applied had a defect density on the order of $2.4 \times 10^4$ defects/cm$^2$, something of a surprising result.

The data from the quartz slide experiment is puzzling, in that the smoother quartz substrate gave a higher defect density after application of a leveling coating than the rougher graphite fiber-epoxy substrate. As there were several weeks between the time that the graphite fiber-epoxy composite data and the fused quartz data were collected, there may have been some aging of the epoxy resin or some increase in the amount of dust that accumulated in the glove box which gave these curious results.

Using the mass of one of the graphite fiber-epoxy samples before and after dipping and the geometry of the sample, this level of improvement is obtained at a weight penalty of 2.5 mg/cm$^2$. Using 0.95 g/cm$^3$ as the density of the cured Epotek 302-1, this corresponds to a thickness of about 26 μm. Leveling coatings of this thickness are comparable to other spray-on leveling coatings reported previously (ref. 7).

Finally, the issue of having a second leveling coating was addressed, along with the added improvement that it provides. Another set of coupons were dipped in the Epotek 301-2. Each coupon was dipped halfway into the epoxy, cured, rotated 90°, dipped halfway into the epoxy again, cured, and coated with 1000 Å of $SiO_2$. In this way, there were four quadrants on each coupon, one quadrant with no leveling coatings, two quadrants with one leveling coating, and one quadrant with two leveling coatings. The results from this series are summarized in table III. From this sample we conclude that the application of a second leveling coating provides no further improvement in defect density population, leaving the sample with about $10^3$ defects/cm$^2$. This result is interesting, in that it may be pointing to a limiting value imposed by the leveling coating technique.

A certain amount of caution needs to be used during the interpretation of leveling coating atomic oxygen durability data. The glove box facility used here was admittedly not comparable to a Class-100 clean room. Dust particles residing in the glove box at the time of the dipping may well have populated the leveling coating, likewise, dust particles may have populated the surface while transporting the samples from the glove box to the e-beam deposition facility. Hence, the data presented here are meant to be used only as a guide. In subsequent work, emphasis ought to be placed on maintaining cleanroom conditions during the critical processing steps of preparing the leveling coating, and the reflective and protective coatings. With additional cleanroom practices, one should expect further improvements in atomic oxygen durability. Perhaps other techniques for applying leveling coatings will also yield a lower defect density population.

## Solar Specular Reflectance

The role of the leveling coating on improving the solar specular reflectance of graphite fiber epoxy composite coupons was also investigated. As mentioned previously, in order to get non-leveling coated and leveling coated solar specular reflectance values on the exact same coupon, it was necessary to first coat the bare graphite epoxy surface with aluminum. After obtaining the solar specular reflectance, the aluminum-coated samples were dipped entirely into the Epotek 301-2, sputter coated with 400 Å of gold and coated with aluminum again. Subsequent solar specular reflectance values were obtained for comparison. The results from this set of experiments are shown in table IV.

Comparing the reflectance of the initial aluminum on the graphite epoxy coupon with the reflectance of the leveling coating, the leveling coating seems to improve the solar specular reflectance from an average value of 0.82 to a value of 0.86, at the expense of the diffuse portion of the reflectivity. Total reflectivity perhaps dropped slightly, from 0.89 to 0.88. These results are similar to those reported previously for Epotek 277 (ref. 1).

Next, aluminum covered samples with and without a leveling coating were exposed to an effective fluence of 2.0x10$^{21}$ atoms/cm$^2$, equivalent to about 0.7 years of solar facing surfaces (not direct ram) at Space Station Freedom altitude. Table V shows that the specular component for the non-leveling coating sample went down from a value of 0.83 to 0.76 while the specular component went down from a value of 0.86 to 0.81 for the leveling coating samples.

It is likely that the leveling coating samples would continue to degrade in solar specular reflectance as a result of atomic oxygen exposure, in a fashion similar to the uncoated samples. The main difference would be in the length of time required to reach the same magnitude of change. More experimentation will be needed to quantify the added performance factor over time.

The atomic oxygen defect density of the reflectance samples cannot be directly compared to those of the $SiO_2$-coated samples cited previously because of the presence of a sputter deposited layer of gold on the reflectance samples. Gold is a catalytic recombinant surface for atomic oxygen. The atomic oxygen recombines to form $O_2$ so that less atomic oxygen is present in the vicinity of the undercut region. For example, Table VI summarizes the defect density of graphite fiber-epoxy samples (from ref. 1) that were aluminum-coated or gold-coated, then exposed to a fluence of 8.32x10$^{20}$ atoms/cm$^2$ of atomic oxygen. Although sputter deposition provides a catalytic surface, it is not conducive to the kind of large scale deposition needed for solar concentrators. Chemical vapor deposition techniques may provide a more thorough coverage resulting in lower defect density values.

## CONCLUSIONS

The use of Epotek 301-2 as a leveling coating provides the designer with essentially two advantages. First, the number of pinhole defect sites on graphite epoxy composite structures coated with an atomic oxygen resistant coating for use in low Earth orbit can be reduced by nearly two orders of magnitude. Additional leveling coatings provide little or no additional protection, suggesting that there is a limiting value to the pinhole population established by the use of leveling coats. It should be noted that the presence of defect sites in a protective coating means that the graphite fiber-epoxy structure will eventually succumb to atomic oxygen attack, however, reducing the number of defect sites will extend the performance lifetime of the graphite fiber-epoxy solar mirror. Perhaps there are other leveling coating application techniques or materials that will yield even lower defect density populations, and longer performance lifetimes.

The second advantage of using a leveling coating is that the leveling coating improves solar specular reflectance of initially rough graphite fiber-epoxy composite mirror surfaces to a value of 0.86. This improvement is consistent with previous studies. The durability of the solar specular reflectance of graphite fiber-epoxy composite mirror surfaces to simulated atomic oxygen attack is also improved, although further experimental work is needed to quantify the extended performance.

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TABLE I. - COMPARISON OF SURFACE ROUGHNESS AFTER APPLYING A SINGLE LEVELING COATING OF VARIOUS EPOXIES.

| Epoxy | Result | Average Roughness (Å) |
|---|---|---|
| Aluminum | n/a | 1500 |
| Epotek 301 | Coating was very thin with a small lip on the end where epoxy had collected. | 1000 |
| Epotek 305 | Coating was similar to 301, but smoother. Short pot life. | 340 |
| Epotek 301-2 | Coating was similar to 305, but some holes were noted on the end where the epoxy had collected. Much longer pot life. | 380 |
| Epotek 377 | The epoxy did not adhere well to the aluminum and had streaks. | 1700 |
| Epotek 314 | Poor surface finish | 3800 |
| Epotek 360 | Poor surface finish | 1500 |

Table II. - DEFECT DENSITY POPULATION OF EPOTEK 301-2 GRAPHITE FIBER-EPOXY COUPONS AND KAPTON WITH NO LEVELING COATING AND ONE LEVELING COATING APPLIED.

| Sample | Fluence | uncoated | coated |
|---|---|---|---|
| Graphite epoxy | $1.93\text{x}10^{21}$ | 70000 defects/cm$^2$ | 3800 defects/cm$^2$ |
| Graphite epoxy | $1.93\text{x}10^{21}$ | 180000 | 1000 |
| Graphite epoxy | $5.78\text{x}10^{21}$ | 140000 | 700 |
| Graphite epoxy | $5.78\text{x}10^{21}$ | 140000 | 200 |
| Quartz | $6.50\text{x}10^{20}$ | ------ | 25000 |

TABLE III. - DEFECT DENSITY POPULATION OF EPOTEK 301-2 GRAPHITE FIBER-EPOXY COUPONS WITH NO LEVELING COATING, ONE LEVELING COATING, AND TWO LEVELING COATINGS APPLIED, EXPOSED TO A FLUENCE OF $2.3\text{x}10^{21}$ ATOMS/CM$^2$.

| no coating | one coating | two coatings |
|---|---|---|
| 210000 | 5700<br>4600 | 7600 defects/cm$^2$ |

Table IV. - SOLAR SPECULAR REFLECTANCE VALUES OF ALUMINUM-COATED GRAPHITE EPOXY COUPONS BEFORE AND AFTER APPLICATION OF A SINGLE LEVELING COATING.

| Aluminum on Pristine Epoxy | | | Aluminum on Leveling Coating | | |
|---|---|---|---|---|---|
| Specular | Diffuse | Total | Specular | Diffuse | Total |
| 0.808 | 0.085 | 0.893 | 0.859 | 0.020 | 0.879 |
| 0.830 | 0.059 | 0.889 | 0.862 | 0.013 | 0.875 |
| 0.806 | 0.081 | 0.887 | 0.861 | 0.015 | 0.876 |

Table V. - SOLAR SPECULAR REFLECTANCE VALUES OF ALUMINUM-COATED GRAPHITE EPOXY COUPONS BEFORE AND AFTER ASHING TO A FLUENCE OF 2.0x10$^{21}$ ATOMS/CM$^2$, ON SAMPLES WITH AND WITHOUT A SINGLE LEVELING COATING.

Aluminum on Pristine Epoxy

| Before ashing | | | After ashing | | |
|---|---|---|---|---|---|
| Specular | Diffuse | Total | Specular | Diffuse | Total |
| 0.837 | 0.060 | 0.897 | 0.763 | 0.094 | 0.857 |
| 0.840 | 0.054 | 0.894 | 0.752 | 0.090 | 0.842 |
| 0.827 | 0.064 | 0.891 | - | - | - |

Aluminum on Leveling Coating

| Before ashing | | | After ashing | | |
|---|---|---|---|---|---|
| Specular | Diffuse | Total | Specular | Diffuse | Total |
| 0.859 | 0.020 | 0.879 | 0.826 | 0.020 | 0.847 |
| 0.862 | 0.013 | 0.875 | 0.817 | 0.015 | 0.832 |
| 0.861 | 0.015 | 0.876 | 0.791 | 0.022 | 0.813 |

Table VI. - DIFFERENCE BETWEEN E-BEAM LINE-OF-SIGHT DEPOSITION AND SPUTTER DEPOSITION ON THE ATOMIC OXYGEN DEFECT DENSITY OF GRAPHITE EPOXY SUBSTRATES, AT AN ATOMIC OXYGEN FLUENCE OF 8.32x10$^{20}$ ATOMS/CM$^2$.

| | |
|---|---|
| Graphite epoxy | 260000 defects/cm$^2$ |
| Graphite epoxy + Al (e-beam) | 22000 defects/cm$^2$ |
| Graphite epoxy + Au (sputter deposition) | 15000 defects/cm$^2$ |
| graphite epoxy + leveling coat + Au | 6000 defects/cm$^2$ |

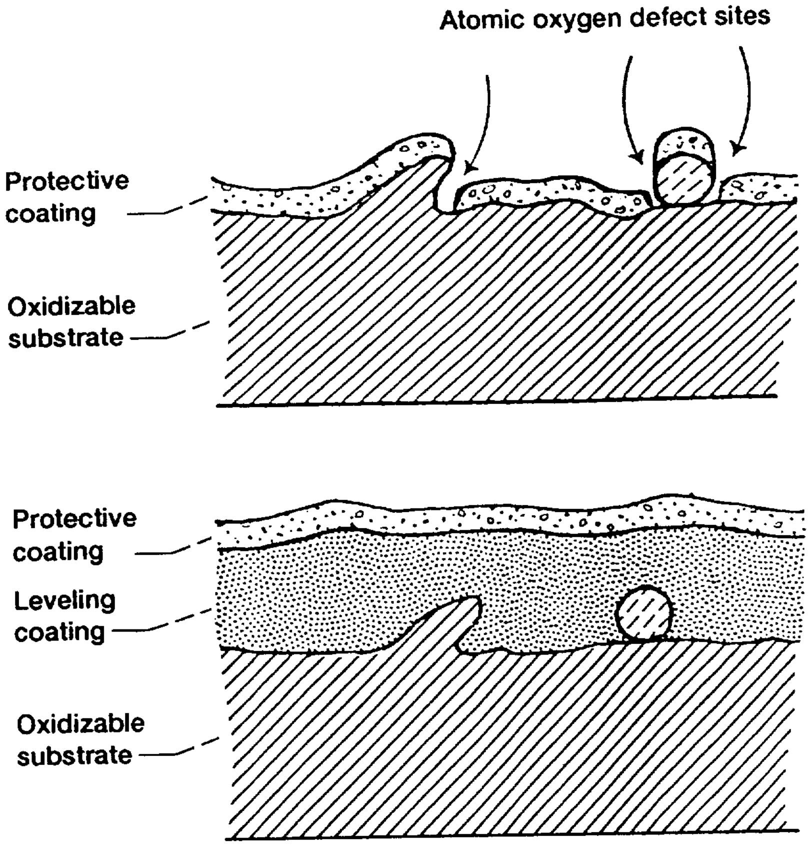

Figure 1.—Schematic diagram showing the role of a leveling coating in reducing atomic oxygen defect density.

Figure 2. Photograph of the dipping apparatus, showing a graphite epoxy composite coupon installed.

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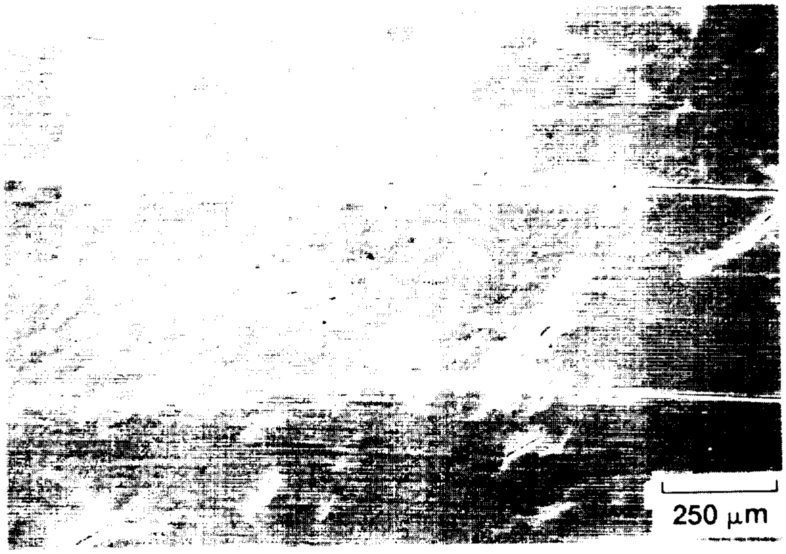
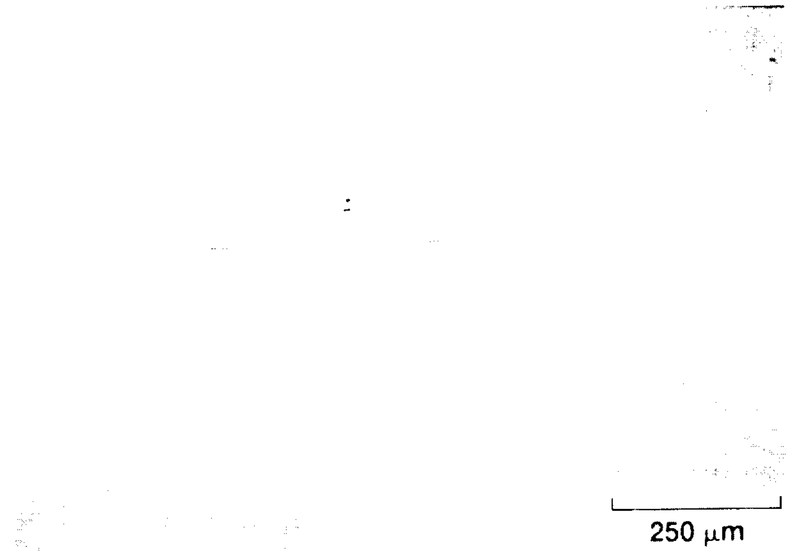


(a) With no leveling coating applied.



(b) With a leveling coating applied.

Figure 3. Scanning electron micrographs of $SiO_2$ coated graphite epoxy composite coupons after exposure to atomic oxygen at a fluence of $1.75 \times 10^{21}$ atoms $cm^2$.