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Durability Issues for the Protection of Materials From Atomic Oxygen Attack in Low Earth Orbit

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DURABILITY ISSUES FOR THE PROTECTION OF MATERIALS FROM ATOMIC OXYGEN ATTACK IN LOW EARTH ORBIT

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ABSTRACT

Low Earth orbital atomic oxygen is capable of eroding most polymeric materials typically used on spacecraft. Solar array blankets, thermal control polymers, and carbon fiber matrix composites are readily oxidized to become thinner and less capable of supporting the loads imposed upon them. Protective coatings have been developed that are durable to atomic oxygen to prevent oxidative erosion of the underlying polymers. However, the details of the surface roughness, coating defect density and coating configuration can play a significant role as to whether or not the coating provides long duration atomic oxygen protection. Identical coatings on different surface roughness surfaces can have drastically different durability results. Examples and analysis of the causes of resultant differences in atomic oxygen protection are presented. Implications based on in-space experiences, ground laboratory testing and computational modeling indicate that thin film vacuum-deposited aluminum protective coatings offer much less atomic oxygen protection than sputter-deposited silicon dioxide coatings.

INTRODUCTION

The use of atomic oxygen protective coatings applied over conventional polymers that have traditionally been used in space has been the primary approach to date to achieve atomic oxygen durability in space. Metal atoms or metal oxide molecules have been used extensively for the protective coating materials. Typically silicon dioxide, fluoropolymer filled silicon dioxide, aluminum oxide, or germanium have been sputter deposited on polymers to provide atomic oxygen protection. For example, the large solar array blankets on International Space Station have been coated with 1300 Å of SiO_2 for atomic oxygen protection.[1]

IN-SPACE PROTECTIVE COATING EXPERIENCES

European Retrievable Carrier (EURECA)

The EURECA spacecraft, which was deployed into low Earth orbit on August 2, 1992 and retrieved on June 24, 1993, was exposed to an atomic oxygen fluence of approximately 2.3×10^{20} atoms/cm^2.[2] To assist in its retrieval, the spacecraft used two thin adhesively mounted acrylic optical retroreflectors for laser range finding. Prevention of atomic oxygen attack of the retroreflector surfaces, which would have degraded the specularity of the reflectance, was accomplished by coating the retroreflector surface with a ~1000 Å thick film of sputter deposited SiO_2 filled with 8 percent fluoropolymer (by volume). The LEO exposed and retrieved retroreflector was inspected and optically characterized.

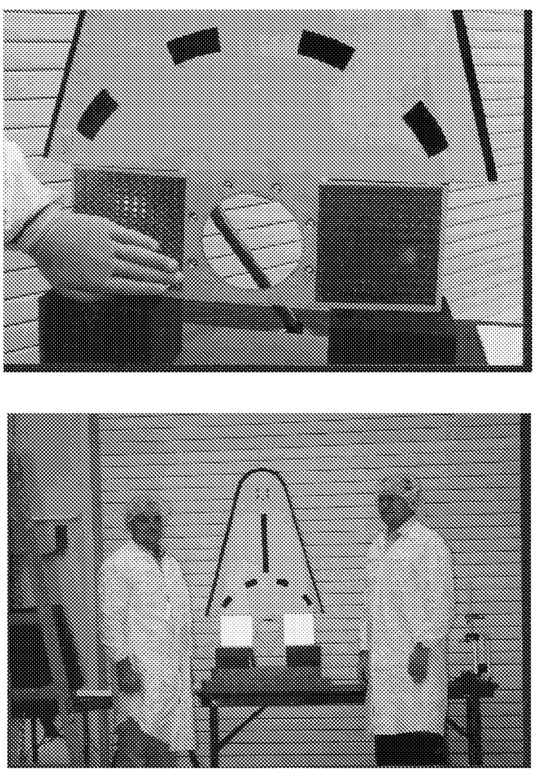


Figure 1. – EURECA retroreflectors after retrieval close up and during illumination.

The results indicated that the protective coating provided excellent protection and the retroreflector performed as planned except in a small 3 cm patch where the protective coating was accidentally abraded prior to flight as a result of handling during preflight ground integration.[3] Figure 1 shows a close up picture of the retroreflectors as well as their appearance during illumination after retrieval.

International Space Station (ISS) Retroreflectors

ISS retroreflectors, which serve in a similar role as the EURECA retroreflectors, employ a glass corner cube retroreflector that is housed in a 10 cm diameter Delrin® 100 polyoxymethylene mount. To prevent atomic oxygen attack of the Delrin®, the machined polymer surfaces were coated by the same processes, in the same facility and with the same ~1000 Å thin film of sputter deposited 8 percent fluoropolymer-filled SiO_2 that was used for the EURECA retroreflector. Several of these retroreflectors have been mounted on the external surfaces of the ISS structures at various locations that are exposed to LEO atomic oxygen. Figure 2 shows a close up of one of the coated retroreflectors prior to use on ISS in space as well as a photograph from space of a retroreflector after attack by atomic oxygen.

It is clear from the in-space photograph that the coating was only partially attached allowing direct atomic oxygen attack of the unprotected areas.

ISS Photovoltaic Array Blanket Box Covers

Prior to deployment, the ISS photovoltaic (PV) arrays were folded into a box that allows the array to be compressed in a controlled manner against a cushion of open pore polyimide foam that was covered with a 0.0254 mm thick aluminized Kapton®

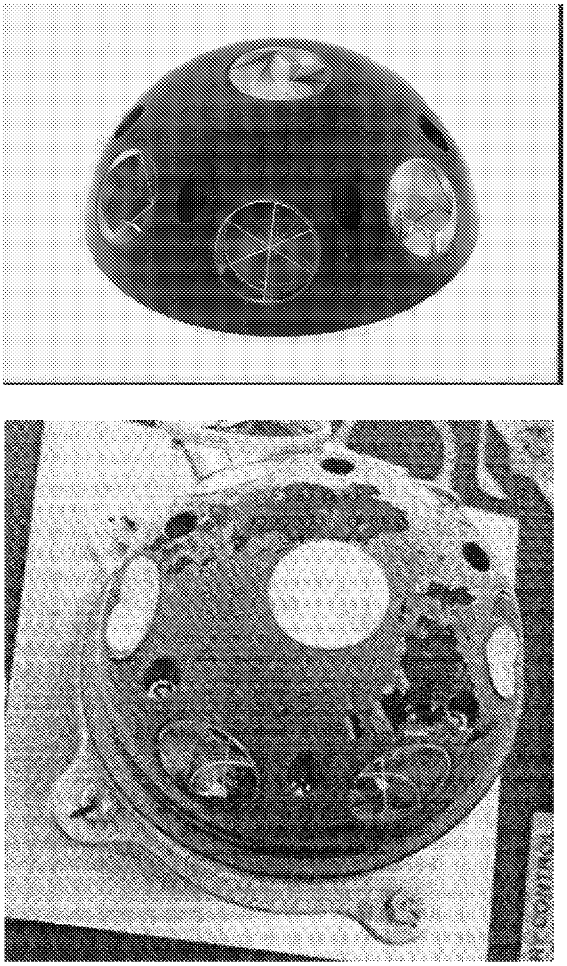


Figure 2. – ISS retroreflectors prior to launch and after atomic oxygen attack during use in space on ISS.

blanket. The Kapton® was coated on both surfaces with 1000 Å of vacuum deposited aluminum. Photographs of the array were taken in orbit, after exposure to atomic oxygen from December 2000 through December 2001, which indicated that the Kapton® blanket had been almost completely oxidized, leaving only the thin largely torn aluminization in place as shown in Figure 3.

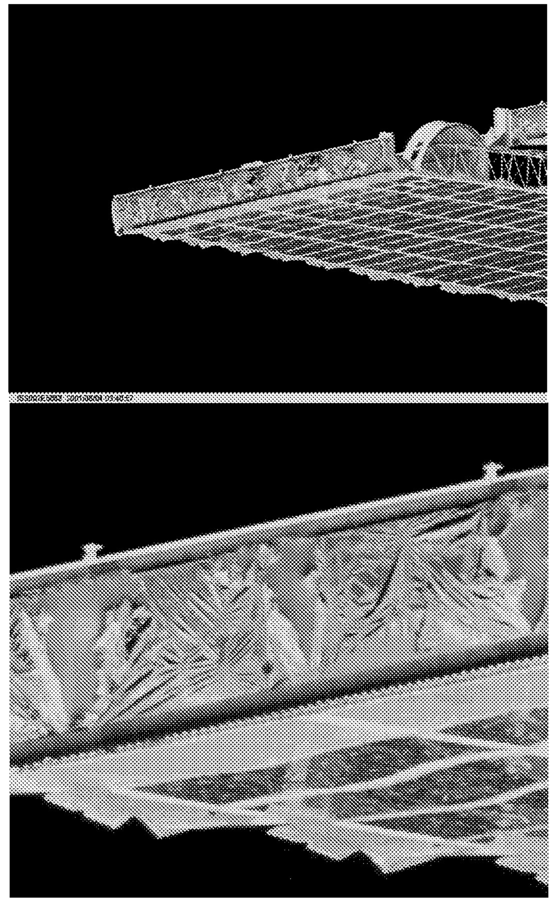


Figure 3. – ISS photovoltaic array blanket box cover after one year in LEO.

ANALYSIS AND DISCUSSION

Surface Roughness and Defect Density

The drastic differences in atomic oxygen protection provided by the same SiO_2 coating filled with 8 percent fluoropolymer on the EURECA retroreflectors and the ISS retroreflectors is thought to be due to drastic differences in the protective coating defect densities. The acrylic EURECA retroreflectors surfaces were extremely smooth as required to produce high fidelity specular reflections. Such smooth surfaces result in low-defect-density protective coatings that have also been demonstrated, in ground laboratory testing, to perform acceptably. For example, smooth surface (air-cured side) Kapton® when coated with 1300 Å thick SiO_2 resulted in ~ 400 pin window defects/cm^2. However, the same coating on the rougher surface (drum-cured side) has been found to result in 3500 pin window defects/cm^2.[1] Similar experiences with graphite epoxy composite surfaces formed by casting against another smooth surface produce defect densities of ~262,300 defects/cm^2.[3] Surface leveling polymers applied over such surfaces have been found to reduce the defect densities by an order of magnitude to ~22,000 defects/cm^2.[3]

The machining of the Delrin® 100 retroreflector mount surfaces produces machine marks or rills in the surface resulting in a highly defected atomic oxygen protective coating. Such rills allow atomic oxygen to oxidize and undercut the high erosion yield Delrin® causing the coating to gradually be left as an unattached gossamer film over the retroreflector mount which could be easily torn and removed by intrinsic stresses and thruster plume loads. The use of smoother surfaces, surface-leveling coatings over the machined Delrin® or use of alternative atomic oxygen durable materials could potentially eliminate the observed problem.

The double-SiO_2 coated ISS solar array blankets may show similar detachment of the outer surface SiO_2 layer with time. However, the defect density appears to be much lower for SiO_2 coated Kapton® than for vacuum deposited aluminum coatings as shown in Figure 4, which compares the experimental results of RF plasma oxidation of double-sided aluminized Kapton® with that of double-sided SiO_2 coated Kapton®.

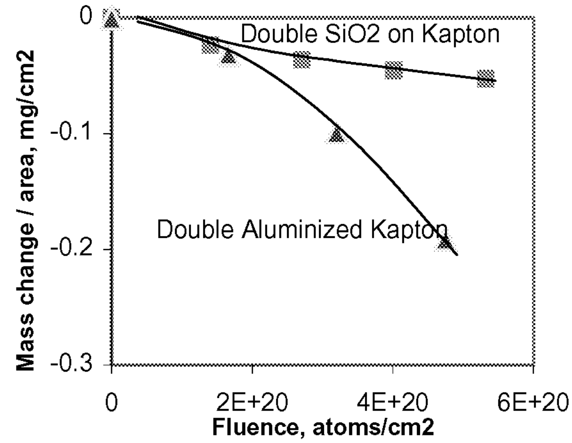
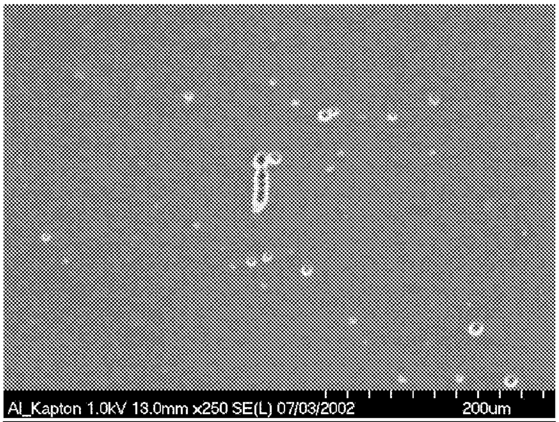


Figure 4. – Comparison of RF plasma oxidation of aluminized and SiO_2 coated Kapton®.

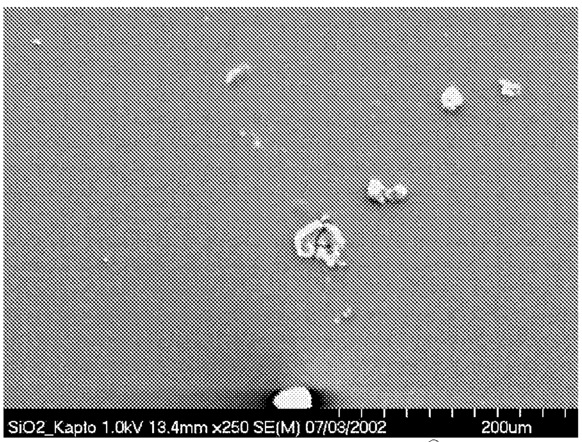
Figure 5 shows corroboration of the much greater defect density of double aluminized Kapton® than that of double SiO_2 coated Kapton®. Scanning electron microscopy (SEM) of the two surfaces after atomic oxygen exposure of the materials in ground laboratory RF atomic oxygen plasmas to an atomic oxygen effective fluence of 3.18×10^{20} atoms/cm^2 followed by tape peeling to remove any unsupported protective coating at defect sites.

As can be seen in Figure 5, the aluminized Kapton® shows evidence of far greater number of defect sites than for the SiO_2 protected Kapton®, where only debris particles are evident on the surface.

Further evidence of the greater number of pin windows in the aluminized coatings can be seen by comparing the water vapor transport through the two protected materials in their pristine condition, as shown in Figure 6.



a. Kapton® that had been aluminized



b. SiO_2 protected Kapton®

Figure 5. – SEM photos of atomic oxygen exposed ISS PV blanket box cover and ISS PV array coated Kapton®.

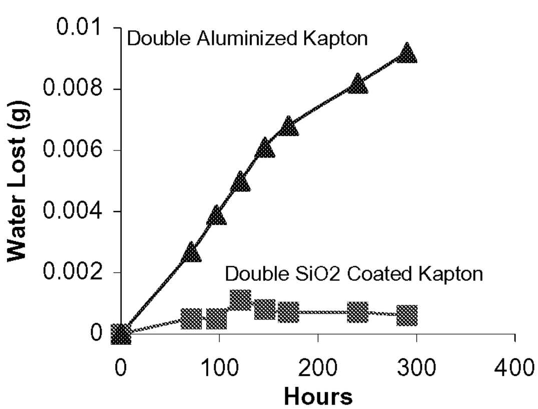


Figure 6. – Water vapor transport rate through protected Kapton®.

Data for Figure 6 was obtained by measuring the weight loss of water filled Petri dishes which had covers made of the pristine ISS PV blanket box cover and ISS PV array coated Kapton® materials. The samples were sealed to the Petri dishes by means of petroleum jelly to minimize moisture loss other than from through the protected polymers. As can be seen there is approximately a factor of 16 greater defect area in the double aluminized Kapton® compared to the double SiO_2 coated Kapton®. When one considers the greater apparent number of defects as well as the greater area of defects, one is lead to consider that the aluminized Kapton® has many more small defects than the SiO_2 coated Kapton®.

Trapping of Atomic Oxygen Between Defected Protective Surfaces

The lack of atomic oxygen protection provided by the aluminized Kapton® blanket cover for the ISS photovoltaic arrays box cushion is thought to be due to the trapping of atomic oxygen between the two aluminized surfaces on the 0.0254 mm thick Kapton® blanket. Defects in the space exposed aluminized surface allow atomic oxygen to erode undercut cavities. If the undercut cavity extends downward to the bottom aluminized surface, then the atomic oxygen becomes somewhat trapped and has multiple opportunities for reaction until it either recombines, reacts, or escapes out one of the defects in the aluminization. This eventually results in a complete loss of the Kapton® with only the aluminized thin film remaining. The vacuum deposited aluminum has a slight tensile stress that causes stress wrinkling of the unsupported aluminum films. Figure 7 is a photograph of a vacuum deposited aluminized Kapton® sample that was placed in a radio frequency plasma environment to completely oxidize the Kapton® over a portion of the sample.

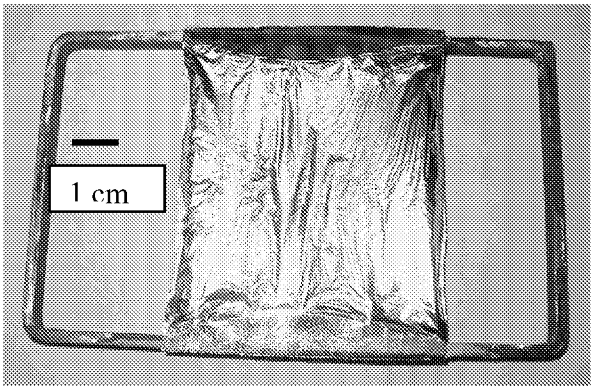


Figure 7. – Photograph of a vacuum deposited aluminized Kapton® sample bonded to a metal frame after ground laboratory oxidation of the Kapton®.

As can be seen in Figure 7, where the ~1000 Angstrom aluminum film in the lower portion of the sample is free standing, stress wrinkles and tears develop similar to those seen in the ISS photograph of Figure 3.

A two dimensional Monte Carlo computational model has been developed which is capable of simulating LEO atomic oxygen attack and undercutting at crack defects in protective coatings over hydrocarbon polymers.[4] Optimal values of the atomic oxygen interaction parameters, listed in Table 1, were identified by selecting values of the parameters that forced the Monte Carlo computational predictions to match results of protected samples retrieved from the Long Duration Exposure Facility.[4]

These interaction parameters and values were used to predict the consequences of atomic oxygen entering a 2-dimensional crack or scratch defect in the top aluminized surface. This was accomplished using 100,000 Monte Carlo atoms entering a defect which was 20 Monte Carlo cells wide (representing a 13.4 micrometer wide defect) over a 38 cell thick (representing a 0.0254 mm thick) Kapton® blanket. Figure 8 compares the Monte Carlo model computational erosion results for a 45-degree angle of attack (relative to the surface normal) of the atomic oxygen for both double surface-coated Kapton® (which was the case for ISS) and single top surface-coated Kapton®.

Table 1. Computational Model Parameters and Reference Values for LEO Atomic Oxygen Interaction with Kapton®

Atomic oxygen initial impact reaction probability	0.11
Activation energy, E_A, in eV for energy dependent reaction probability	0.26
Atomic oxygen probability angle of impact dependence exponent, n, in $(\cos\theta)^n$ angular dependence where θ is the angle between the arrival direction and the local surface normal	0.5
Probability of atomic oxygen recombination upon impact with protective coating	0.13
Probability of atomic oxygen recombination upon impact with polymer	0.24
Fractional energy loss upon impact with polymer	0.28
Degree of specularity as opposed to diffuse scattering of atomic oxygen upon non-reactive impact with protective coating where 1 = fully specular and 0 = fully diffuse scattering	0.4
Degree of specularity as opposed to diffuse scattering of atomic oxygen upon non-reactive impact with polymer where 1 = fully specular and 0 = fully diffuse scattering	0.035
Temperature for thermally accommodated atomic oxygen atoms, K	300
Limit of how many bounces the atomic oxygen atoms are allowed to make before an estimate of the probability of reaction is assigned	25
Thermally accommodated energy/actual atom energy for atoms assumed to be thermally accommodated	0.9
Initial atomic oxygen energy, eV	4.5
Thermospheric atomic oxygen energy, K	1000
Atomic oxygen arrival plane relative to Earth for a Maxwell-Boltzmann atomic oxygen temperature distribution and an orbital inclination of 28.5°	Horizontal

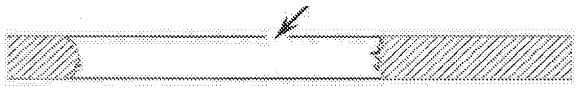


Figure 8. – Monte Carlo computational atomic oxygen erosion predictions for a 45 degree from perpendicular angle of attack of atomic oxygen at a crack or scratch defect in the aluminized Kapton® surface.

As can be seen from Figure 8, even though the atomic oxygen gradually becomes less energetic with the number of interactions and has approximately a 13% chance of recombination, the trapped atoms undercut far more in the actual ISS case of a double aluminization as would have occurred if the Kapton® was simply aluminized on one side. Thus, contrary to intuition, the use of two atomic oxygen protective coatings rather than a single coating appears to cause more rather than less undercutting attack.

The extent of undercutting of trapped atomic oxygen is also dependent on the opportunity for the atoms to lose energy, recombine, or escape back out the defect opening.

Figure 9 shows the results of 2-dimensional Monte Carlo computational modeling predictions for a 45-degree angle of attack atomic oxygen on a 13.4 micrometer wide crack or scratch in the protective coating for both single side and double side aluminized Kapton®.

As can be seen in Figure 6, initially, as the undercutting starts the existence or absence of the back surface coating plays no role and as the cavity grows the probability of atoms reacting increases due to trapping of the incoming atom. However, when the undercutting reaches the bottom surface, atoms arriving at the plane of the bottom can either escape (in the case of no bottom protective coating) or have a chance or scattering with reduction in energy through partial thermal accomidation or recombine (in the case of the a bottom surface protective coating). The modeling indicates that the double surface aluminized Kapton® consistently reacts about twice as many atomic oxygen atoms as the single surface aluminized Kapton® except at very low fluences where the erosion in either case does not reach the bottom of the polymer. Thus, it appears that a single surface aluminized Kapton® would have been much more durable because the unreacted atoms passing through the bottom of the polymer would simply enter into the open pore foam and gradually react with it, without causing much damage to the aluminized Kapton®.

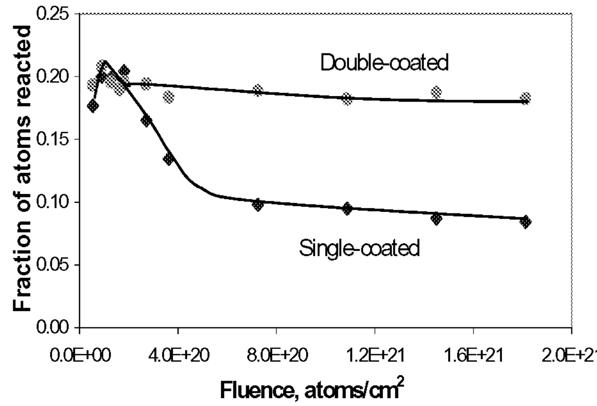
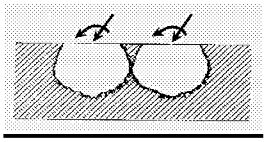
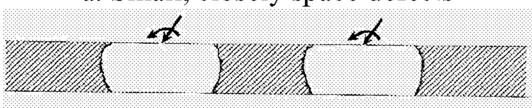


Figure 9. – Computational atomic oxygen erosion predictions for 45-degree incident atomic oxygen attack at crack or scratch defect sites on protected Kapton®.

Based on the data that indicates that the aluminized protective coating may have many small defects, a Monte Carlo computational comparison was made between protective coatings that had the same fractional defect area but varied in the



a. Small, closely space defects



b. Wide, more separated defects

Figure 10. – Monte Carlo predictions comparing the same fractional crack defect areas but different defect sizes.

width of the crack defect in the protective coating. The comparison of resulting undercut cavities is shown in Figure 10 which compares the undercut cavities under LEO sweeping atomic attack conditions. Each configuration was run to the same fluence level.

As can be seen from Figure 10, the undercut cavity for the closely spaced small defects touch each other which would allow the upper portion of the blanket to become detached and even more vulnerable to atomic oxygen attack. However the wide but more separated defected configuration would only have occasional holes in it.

The Monte Carlo computational model can be used to compute the critical atomic oxygen fluence needed to create touching or connecting under cut cavities as a function of defect size for constant fractional defect areas (the ratio of defect area to total surface area). The resulting prediction for fractional defect areas of 0.0257 is shown in Figure 11.

As one can see, the critical fluence, which will allow the upper surface of the blanket to become detached, drops rapidly with defect width for small defects. Thus, if the aluminized surface contains many very small defects, the connection of under cut

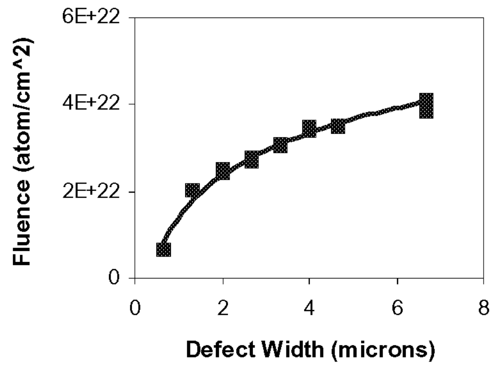


Figure 11. – Computational atomic oxygen prediction of critical fluence for fractional defect areas of 0.0257.

cavities will begin to occur at much lower fluences that if the defects were larger and more separated.

CONCLUSIONS

Atomic oxygen protective coatings have been developed and used in space that performs acceptably. However, rough surface substrates cause defects in the protective coatings that allow atomic oxygen to react and gradually undercut the protective coating. In the case of machined Delrin® ISS retroreflector mounts, such roughness has lead to detachment of portions of the protective film covering the retroreflector mount.

Atomic oxygen undercutting of the double aluminized Kapton® blanket covers for the ISS photovoltaic array box cushions has occurred resulting in a torn and partially detached aluminum film. Based on computational modeling, and ground laboratory characterization testing, early failure of the aluminized Kapton® ISS PV blanket box covers can be caused by excessive atomic oxygen attack resulting from the presence of many small defects in the aluminization in comparison to many fewer defects in the double SiO_2 coated Kapton®. High defect area, defect density and the application of the protective coating to both sides of the aluminized Kapton® ISS PV blanket box covers appear to have contributed to the early failure of the covers as indicated by ground laboratory atomic oxygen testing, SEM, moisture transmission and Monte Carlo computational modeling. The use of a protective coating on only the exposed side of the Kapton® blanket may increase the durability of the blanket.

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