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Atomic Oxygen Protection of Materials in Low Earth Orbit

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ATOMIC OXYGEN PROTECTION OF MATERIALS IN LOW EARTH ORBIT

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ABSTRACT

Spacecraft polymeric materials as well as polymer-matrix carbon-fiber composites can be significantly eroded as a result of exposure to atomic oxygen in low Earth orbit (LEO). Several new materials now exist, as well as modifications to conventionally used materials, that provide much more resistance to atomic oxygen attack than conventional hydrocarbon polymers. Protective coatings have also been developed which are resistant to atomic oxygen attack and provide protection of underlying materials. However, in actual spacecraft applications, the configuration, choice of materials, surface characteristics and functional requirements of quasi-durable materials or protective coatings can have great impact on the resulting performance and durability. Atomic oxygen degradation phenomena occurring on past and existing spacecraft will be presented. Issues and considerations involved in providing atomic oxygen protection for materials used on spacecraft in low Earth orbit will be addressed. Analysis of in-space results to determine the causes of successes and failures of atomic oxygen protective coatings is presented.

1. INTRODUCTION

Atomic oxygen, which is the most prevalent of the atmospheric species in LEO, can readily oxidize spacecraft polymers as a result of its high reactivity and high flux (1–3). Such oxidation can result in erosion leading to serious spacecraft performance and/or structural failure problems. Efforts have been expended by numerous aerospace and materials organizations to develop protective coatings for polymers as well as polymeric materials that are inherently durable to atomic oxygen attack. The development of both protective coatings for polymers as well as inherently durable polymers has been predominantly through the use of metal atoms that develop stable nonvolatile oxides thus preventing or reducing atomic oxygen attack of the hydrocarbon polymers.

Quasidurable materials have been explored or developed which incorporate silicone along with polyimides with the intent of atomic oxygen caused formation of sufficient silicon dioxide surface populations to protect the underlying polymers. DuPont has explored a polydimethylsilioxane-polyimide mixture in a material called AOR Kapton (Atomic Oxygen Resistant Kapton) (4). However, the spatial varying and low concentration of the silicone constituents allows gradual atomic oxygen attack of the bulk material when evaluated in ground laboratory testing (4). Polydimethylsilioxanes, which contain one silicon atom per oxygen atom, are gradually converted to silica by the atomic oxygen attack. In this process the loss of the methyl groups and conversion to SiO_2 results in shrinkage of the polymer with attendant cracks that can lead to attack of any underlying polymers (5–6). However, the use of textured surfaces on the polydimethylsilioxanes has produced coatings that do not crack from the same atomic oxygen fluences that would cause the smooth surfaces on the same materials to crack (7). Silsesquesilioxanes have shown promise over conventional polydimethylsilioxanes in that they contain 1.5 silicone atoms per oxygen atom and do not show the shrinkage cracking phenomena of polydimethylsilioxanes. Silsesquesilioxane-polyimide copolymers are currently being investigated by the University of Michigan that have potential to satisfy necessary mechanical properties, processing characteristics as well as atomic oxygen durability properties (8). The incorporation of other metal atoms in polyimide compounds has also been investigated. Triton Systems, Inc. has developed phosphorous containing polyimides in both amber and clear colors which develop phosphorous oxides on the surface of the polymer that tend to shield the underlying polymers from atomic oxygen attack (9). Such polymers are currently being evaluated in space as part of the Materials International Space Station Experiment. University of Rochester has developed zirconium complex compounds that can be mixed with polyimides that tend to develop protective zirconium oxide surfaces (10). Some of the challenges of the above materials have been to incorporate a sufficient atomic population of the protecting metal atoms in the polymer structures to become atomic oxygen protecting without compromising their mechanical, optical, and ultraviolet radiation durability properties. Testing of many of these materials has yet to be completed to validate their long-term durability in the LEO environment.

The use of atomic oxygen protective coatings over conventional polymers that have been used in space seems to be an easier solution to obtaining atomic oxygen durability in space based on the extent of use of this approach to date. Metal atoms or metal oxide molecules have been used extensively for surface protection. Typically silicone 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 Angstroms of SiO_2 for atomic oxygen protection (11).

Surfaces of hydrocarbon polymers have been modified by Integrity Testing Laboratory using chemical conversion to incorporate silicon atoms for protection in a silylation process or by implanting metal atoms of Al, Si or B in the surface of polymers for the purpose of developing protective oxides (12). These materials are also currently being tested in space as part of the Materials International Space Station Experiment.

Although protective coatings can provide excellent atomic oxygen protection of hydrocarbon or halocarbon polymers, the details of how the coatings are used and/or applied can result in widely varying protection consequences.

2. IN-SPACE PROTECTIVE COATING EXPERIENCES

2.1 European Retrievable Carrier (EURECA)

The EURECA spacecraft, which was deployed into low Earth orbit on August 2, 1992 and retrieved after 11 months on June 24, 1993, was exposed to an atomic oxygen fluence of approximately 2.3×10^{20} atoms/cm^2 (13). 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 Angstrom thick film of sputter deposited SiO_2 filled with 8% fluoropolymer (by volume). The LEO exposed and retrieved retroreflector was inspected and optically characterized. 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 (13). Figure 1 shows a close up picture of the retroreflectors as well as their appearance during illumination after retrieval.

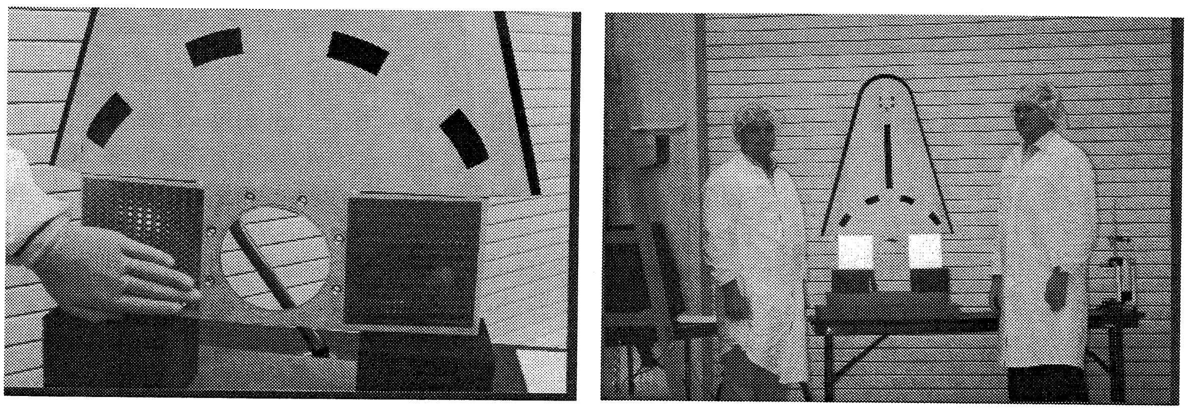


Figure 1. – EURECA retroreflectors after retrieval close up and during illumination.

2.2 International Space Station (ISS) Retroreflectors

ISS retroreflectors, which serve in a similar role as the EURCA retroreflectors, have been used which employ a corner cube retroreflector that is housed in a 10 cm diameter Delrin® 100 polyoxymethylene mount. Polyoxymethylene is an oxygen rich polymer that results in it being readily attacked by atomic oxygen. 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 Angstrom thin film of sputter deposited of 8% 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.

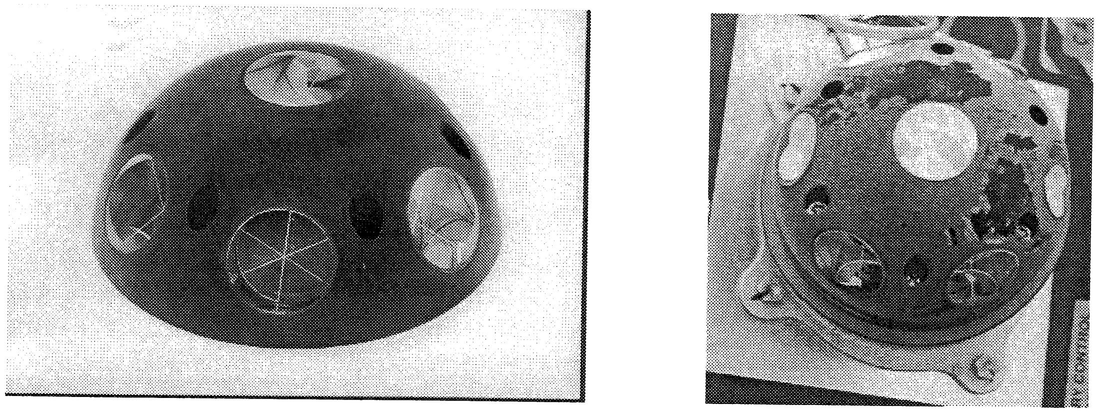
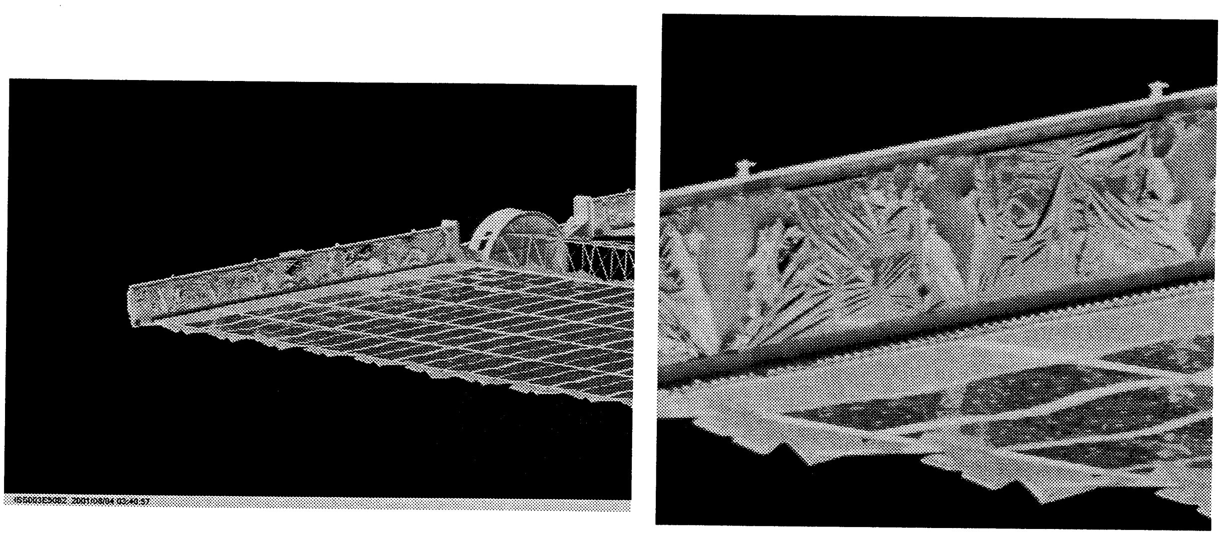


Figure 2. – ISS retroreflectors prior to launch and during use in space on ISS after atomic oxygen attack.

2.3 ISS Photovoltaic Array Blanket Box Lid Blanket

Prior to deployment, the ISS photovoltaic arrays were folded into a box that allows the array to be compressed in a controlled manner against a cushion of open pore polyimide that was covered with a 0.0254 mm thick aluminized Kapton® blanket. The Kapton® was coated on both surfaces with 1000 Angstroms of vacuum deposited aluminum. The array was exposed to the LEO atomic oxygen environment from December 2000 through December 2001. Photographs of the array, taken in orbit, indicated that the Kapton® blanket had been almost completely oxidized leaving only the thin largely torn aluminization in place as shown in Figure 3.



a. Distant photo

b. Close up photo

Figure 3. – ISS photovoltaic array showing effects of atomic oxygen erosion of the double aluminized Kapton® blanket cover for the ISS photovoltaic arrays box cushions.

3. ANALYSES AND DISCUSSION

3.1 Surface Roughness and Defect Density

The drastic differences in atomic oxygen protection provided by the same SiO_2 coating filled with 8% 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 Angstrom 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 (11). Similar experiences with graphite epoxy composite surfaces formed by casting against another smooth surface produce defect densities of ~262,300 defects/ cm^2 (14). 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 (14).

The machining of the Delrin® 100 polyoxymethylene 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 surface leveling coatings over the machined Delrin® or use of alternative atomic oxygen durable materials could potentially eliminate the observed problem.

3.2 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 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 4 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.

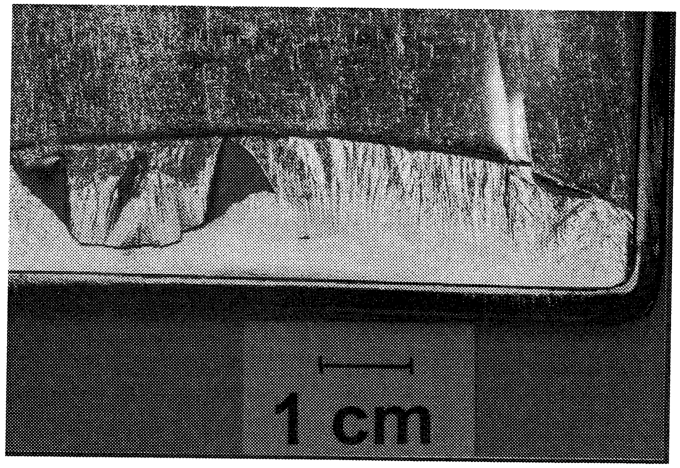


Figure 4. – Photograph of a vacuum deposited aluminized Kapton® sample after ground laboratory oxidation of lower portion of the sample.

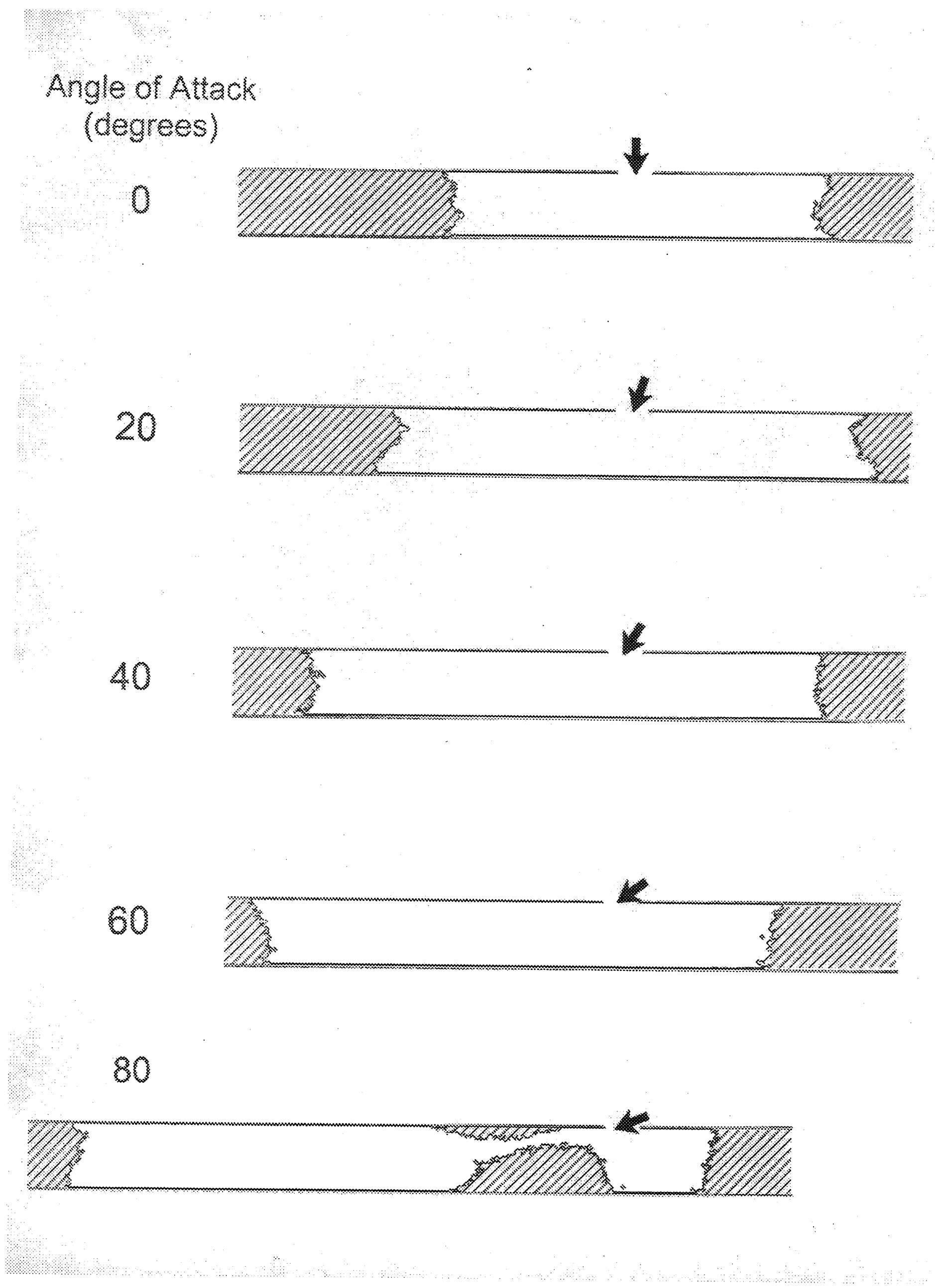
As can be seen in Figure 4, where the ~1000 Angstrom aluminum film in the lower portion of the sample is free standing, stress wrinkles and tears develop similar to those seen in the ISS photograph of Figure 3.

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 (15). Optimal values of the atomic oxygen interaction parameters have been identified (see Table 1) by forcing the Monte Carlo computational predictions to match results of protected samples retrieved from the Long Duration Exposure Facility (15).

The Monte Carlo model interaction parameters and values indicated in Table 1 were used to predict the consequences of the same fluence (100000 Monte Carlo atoms) of atomic oxygen entering a crack or scratch defect in the top aluminized surface. This was accomplished using 100000 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 5 shows the Monte Carlo model computational erosion results for various angles of attack of the atomic oxygen for both double surface-coated Kapton® (which was the case for ISS) and the predicted result if only a single top surface had been aluminized.

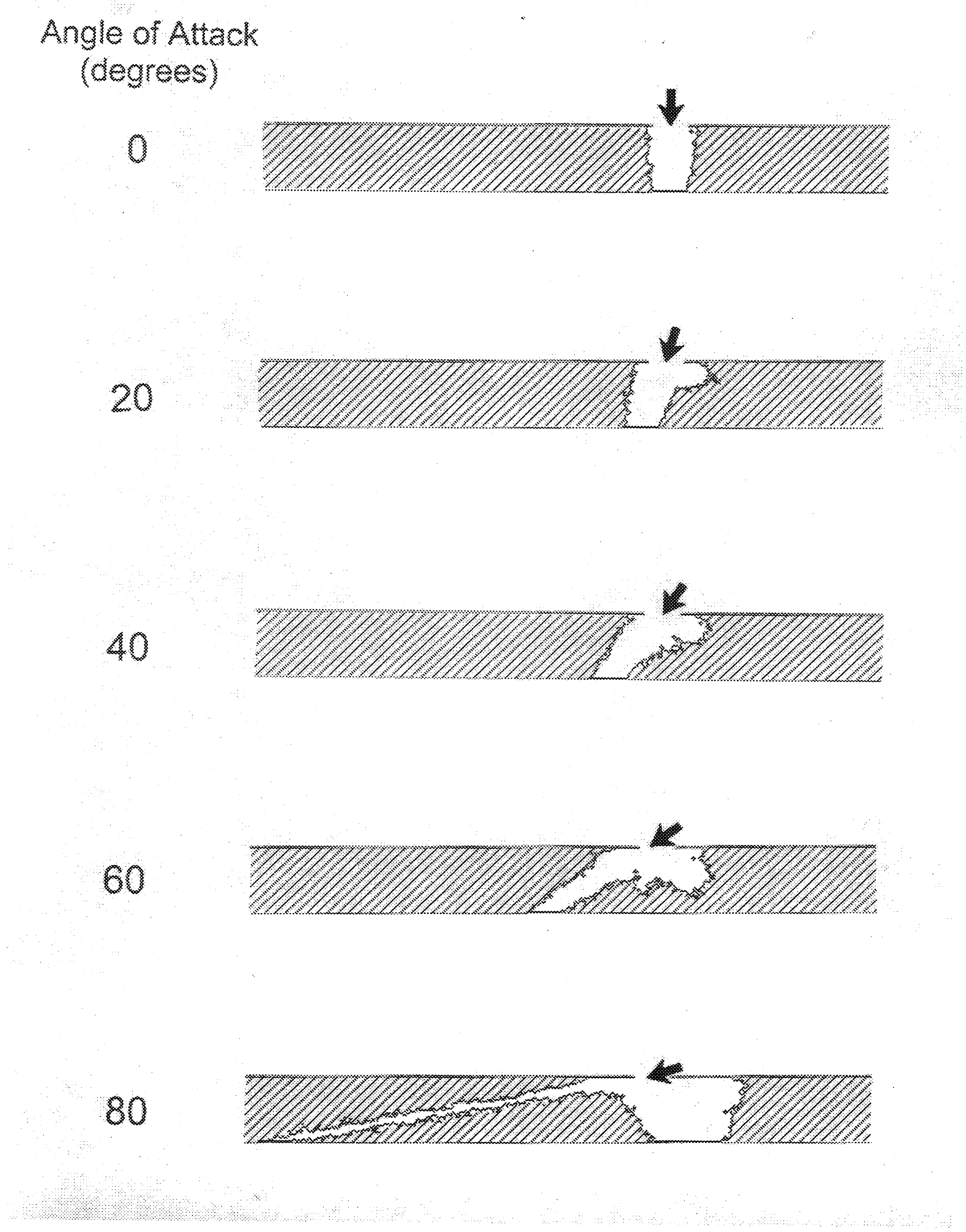
Table 1. Computational Model Parameters and Reference Values for LEO Atomic Oxygen Interaction with Kapton®

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
Atomic oxygen average arrival direction with respect to initial surface normal, degrees	Depends upon example
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



a. Aluminized on both sides

Figure 5. – Monte Carlo computational atomic oxygen erosion predictions for various angles of attack of atomic oxygen at a crack or scratch defect in the aluminized Kapton® surface.



b. Aluminized on exposed side only

Figure 5. – Monte Carlo computational atomic oxygen erosion predictions for various angles of attack of atomic oxygen at a crack or scratch defect in the aluminized Kapton® surface.

As can be seen from Figure 5 and Table 1, even though the atomic oxygen gradually becomes less energetic with number of interactions and has 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 it was simply aluminized on one side. Thus, more atomic oxygen protective coatings appear to cause more attack than if simply a single coating was used.

The extent of undercutting of trapped atomic oxygen is also dependent on the opportunity for the atoms to loose energy, recombine or escape back out the defect opening. Figure 6 compares the results of Monte Carlo computational predictions for sweeping incidence (variable angle of attack) atomic oxygen using 100000 Monte Carlo atoms entering a 13.4 micrometer wide crack or scratch defect for both single side and double side aluminized Kapton®.

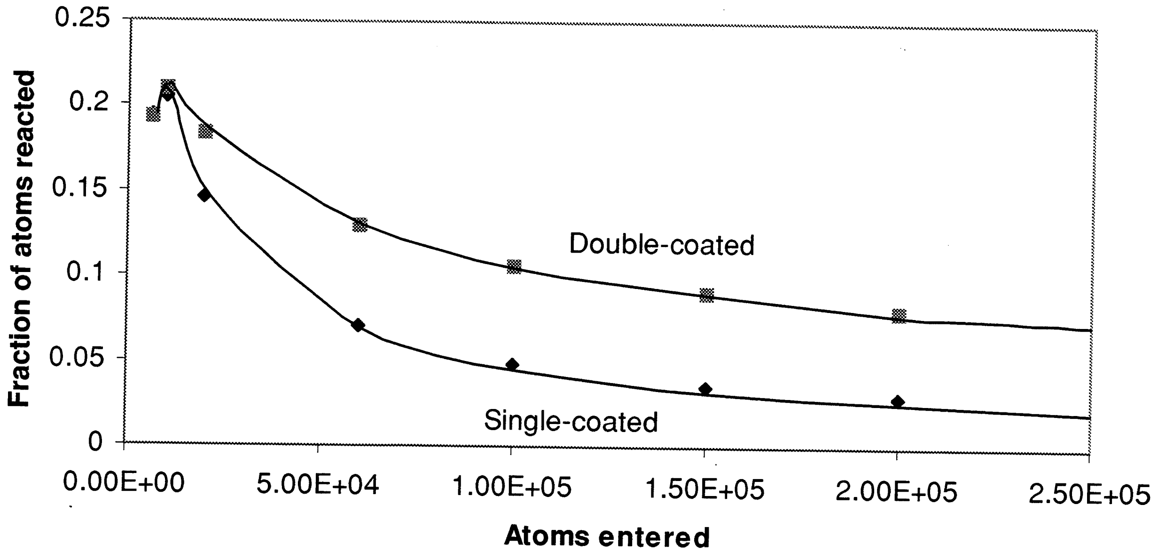


Figure 6. – Monte Carlo computational atomic oxygen erosion predictions for sweeping incidence atomic oxygen attack at crack or scratch defect sites in the aluminized Kapton® as a function of atomic oxygen fluence.

As can be seen in Figure 6, the double surface aluminized Kapton® consistently reacts more atomic oxygen atoms than the single surface aluminized Kapton® except at very low fluences where the erosion in both cases do not reach the bottom of the polymer. For both cases, as the fluence increases, the atomic oxygen can escape out the bottom (only in the case of the single surface aluminized Kapton®), recombine or thermally accommodate and thus becomes less probable to react with the Kapton®. 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 simply enter into the open pore foam and would gradually react with it without causing much damage to the aluminized Kapton®.

One might also wonder why the double SiO_2 coated ISS solar array blankets have not shown similar detachment of the outer surface SiO_2 layer. However, considerable efforts were expended to reduce the defect density in these surfaces which have probably resulted in there being far fewer defects/cm^2 in the solar array blanket coatings than for the aluminized blankets on the solar array blanket boxes. Ground laboratory testing to full 15-year ISS fluence levels also indicated acceptably low undercutting.

4. CONCLUSIONS

Atomic oxygen protective coatings have been developed and used in space that perform 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 Monte Carlo modeling, it appears that this is a result of atomic oxygen atoms that become trapped between the two aluminized films on each side of the Kapton® blanket. Thus it appears that use of a single top surface aluminum coating would result in improved atomic oxygen durability.

For both the ISS retroreflector mounts and the aluminized Kapton® blanket covers for the ISS photovoltaic arrays box cushions, ground laboratory testing should validate durability improvements.

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